Spatial and temporal water quality in the River Esk in relation to freshwater pearl mussels

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Declaration

This thesis is the result of my own work and has not been submitted for consideration in any other examination. Material from the work of other authors, which is referred to in the thesis, is acknowledged in the text.

Statement of copyright

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Abstract: Spatial and temporal water quality in the River Esk in relation to freshwater pearl mussels (David Balmford)

Riverine systems provide networks of habitats, resources and biodiversity. Globally, riverine biodiversity is under threat due to a variety of human activities; diffuse pollution, particularly in agricultural catchments, raises challenges to river environments. This work addresses the water quality in the River Esk (North York Moors National Park) and its impact on biodiversity, namely the rare, declining population of freshwater pearl mussels (*Margaritifera margaritifera*). Water quality parameters were monitored both spatially and temporally and the drivers of water quality were investigated. Monthly sampling was undertaken at twenty sites within the Esk catchment. High-resolution monitoring was enabled by three autosamplers and two pressure transducers, which allowed for assessment of the water quality at both baseflow and stormflow. Anion and cation analysis were conducted on all samples and field-based characterisation furthered by use of a YSI multi-parameter probe.

Results revealed a number of concentration hotspots with values of nitrate that are thought unsuitable for freshwater pearl mussels. Other water quality variables were all within acceptable limits. Concentrations of nitrate in sub-catchments with smaller upstream areas proved to be more variable than in larger catchments. Land cover was found to be a key driver of concentration: high upstream percentage of improved pasture resulted in high nitrate concentration; high upstream percentage of moorland resulted in low nitrate concentration. During storm events, concentrations of key parameters were greater than limits suggested for pearl mussels (nitrate up to approximately 3.0 mg l^{-1} as opposed to limit of 1.0 mg l^{-1} proposed by Skinner *et al.* (2003)); this raised the fundamental question of exposure time. The process of connectivity was considered by the application of the risk-based hydrological model SCIMAP. This highlighted a number of areas that could adversely affect the pearl mussel population; these results will require further validation. Empirical work provided a foundation for future management recommendations. A case is made for the importance of expansion or addition of riparian buffer zones. This study demonstrates the importance of obtaining high-resolution data sets to understand habitat quality. The worth of these data is demonstrated in planning interventions in catchments to enable the Water Framework Directive (WFD) and UK Biodiversity Action Plan (BAP) standards to be met.

Contents

List of Figures

2. Literature Review

3. Methodology and sites outline

4. Spatial variations in water quality parameters in the River Esk

5. Temporal variation in water quality in the River Esk

7. Discussion

List of Tables

3. Methodology and sites outline

4. Spatial variations in water quality parameters in the River Esk

5. Temporal variation in water quality in the River Esk

6. Discussion

7. Discussion

1.0 Introduction

1.1 Research Background

Rivers provide an array of ecosystem goods and services, including biodiversity, attenuation of flood waters, abstraction, recreation, production of power, food and other marketable goods. However, human activities in river catchments over prolonged periods, such as settlement, agriculture and forestry, impact the freshwater ecosystem and have substantially altered riverine processes (Malmqvist and Rundle, 2002). This has culminated in altered flow regimes, sources of point and diffuse pollution and widespread degradation, with negative consequences for biodiversity.

The importance of river pollution has been increasingly recognised in recent years and is provoking a response both in terms of international legalisation, such as the Water Framework Directive (WFD- 2000/60/EC); and conservation priorities, such as The International Decade for Action 'Water for Life' (2005-2015). The WFD has the intent to achieve good ecological and chemical status of UK waterways by 2015 (Environment Agency, 2006). The result has been considerable efforts (both voluntary and under obligation) to reverse this scenario.

However, despite conservation efforts, 'extensive nutrient enrichment' (Dudgeon *et al.* 2005) remains a pandemic issue that is worsening as nutrient fluxes are altered (Smith, 2003), particularly driven by agricultural intensification (Matson *et al.* 1997). Furthermore, little is known about how chronic and acute disturbances influence biota, how resilient various organisms and the river ecosystems are to such disruptions, or how institutions respond to potential loss of biodiversity. This raises a fundamental question, specifically in terms of management practices, 'What can be done in freshwater environments to improve the state of ecosystems to protect and rehabilitate biodiversity?' Research to address this question is valuable to conservation agencies but also more widely to aquatic ecosystems.

Despite the perception that terrestrial species are under significant threat of extinction, it is freshwater species that are in greater peril (Ricciardi and Rasmussen, 1999; Richter *et al.* 1997). There is a global threat to freshwater biodiversity driven by a number of factors: overexploitation; water pollution; flow modification; degradation or removal of habitat; and the effects of invasive species (Dudgeon *et al.* 2005; Malmqvist and Rundle, 2002). These anthropogenic factors can be linked to the desire to meet the needs of an increasing global population (e.g. Gleick *et al.* 2003). This is forming 'alarming trends' (Ricciardi and Rasmussen, 1999) and now no aquatic environment can even claim to be ‘pristine’ with the anthropogenic influence inducing change upon both the climate and environment (Edwards and Withers, 2008). The interaction of these factors has directly and/or indirectly impacted populations of freshwater species (Dudgeon, *et al.* 2005).

The freshwater pearl mussel population in the River Esk, in the North York Moors National Park (North-East England), provides an opportunity for an investigation into water quality and biodiversity. Water quality and life cycles of freshwater pearl mussels need to be investigated synchronously in order to understand the influence of catchment processes on habitat quality in rivers. Monitoring needs to capture temporal variations (both seasonal and changes in discharge addressing floods and droughts) in conjunction with spatial variations in factors influencing habitat quality. Land use change, including resulting changes in water quality and silt supply, is seen as one of the major threats to global biodiversity (Sala *et al.*, 2000; Walling and Collins, 2008). Research has focussed on understanding and predicting diffuse nutrient inputs in catchments (Heathwaite *et al.*, 2005a; Lane *et al.*, 2004; Deasy *et al.*, 2009), but this has not been explicitly linked to river habitat quality or biodiversity. For example, how varying land use patterns within a catchment dictate the nutrient release to the watercourse and implications this presents for freshwater pearl mussel habitat and recruitment.

1.2 Study rationale

The rationale of this study is that in the River Esk the population of freshwater pearl mussels are under threat of extinction as there are no juveniles within the river. The North York Moors National Park Authority (NYMNPA) (stakeholders in this research) and Environment Agency, who have the backing of local farmers, are keen to preserve the pearl mussel to prevent its extinction within the river and preserve the mussels which are part of the Esk’s natural ecosystem and the cultural heritage of the North York Moors region. Previous research has centred on fine sediment fluxes in the catchment (Bracken and Warburton, 2005) and the problem has been linked to siltation of the salmon redds. However, recent research suggests that water quality may also have an important impact on the species’ success (Bracken, 2009). Therefore, a detailed assessment of the Esk will be undertaken to investigate how water quality varies in the catchment in both time and space. This work will contribute to the evidence and research priority regarding the minimum water quality requirements that are suitable for pearl mussel habitat.

1.3 Aim and objectives

To address this rationale this research aims:

to assess spatial and temporal trends in water quality within the Esk in relation to the freshwater pearl mussel population and suggest potential management opportunities to aid conservation.

The following objectives have been adopted in order to meet this aim:

1. To collect and analyse spatial and temporal water quality parameters in the Esk catchment using a point sampling network and autosampler monitoring stations.
2. To test the (null) hypothesis that: a) land use and; b) catchment area do not determine water quality in the Esk catchment.
3. To demonstrate the value of a high-resolution dataset to illustrate the ecological status of a river basin system to map on to management expectations.
4. To suggest methods to improve the water quality to help efforts to conserve freshwater pearl mussels.

1.4 Thesis Outline

This chapter has presented an overview of the central issues onto which this work maps and provides a framing for what follows. Chapter 2 expands this framing to highlight the literature key to this work; water quality patterns and processes, management and freshwater pearl mussels. The following chapter summarises the methods used in this study. Chapters 4 and 5 display the spatial and temporal results respectively. Chapter 5 utilises data from automatic samplers to look at the impact of increasing stage on the water quality. In Chapter 6 the evidence is applied to the whole catchment using a hydrological risk model, SCIMAP, to provide an estimate of risk hot spots. Chapter 7 draws together the evidence gathered and analysed in the previous chapters; it addresses management options as well as the implications for the population of freshwater pearl mussels in the River Esk. Finally, Chapter 8 concludes this work and discusses its limitations and suggests further work that could be addressed in the future.

2.0 Literature Review

2.1 Introduction

This chapter provides an overview of the literature relevant to this thesis. Initially the key understandings of water quality will be discussed (section 2.2), followed by an investigation of management expectations and mechanisms (section 2.3). Then freshwater pearl mussels are discussed (section 2.4) particularly in respect to water quality (section 2.4.1) and the case study catchment population in the River Esk in the North York Moors National Park, North East England is introduced (section 2.4.2).

2.2 Water Quality: current understandings

To begin to understand how water quality interacts with ecosystem biodiversity, is it vital to build upon the relevant knowledge of water quality and catchment dynamics. Pollution of water can be divided into two key elements: point-source pollution and non-point pollution. Point sources as defined by Novotny (2003) are 'any discernable, confined and discrete conveyance, including but not limited to, any pipe, ditch, channel...not including agricultural storm water and return flow from irrigated agriculture' (Edwards and Withers, 2008: 145). Therefore, point-source pollution sources can be identified and controlled to a greater extent. Indeed in recent years, efforts to improve water quality have focussed on these sources, which has led to an improvement but has also uncovered the previously concealed influence of non-point sources, or diffuse pollution sources, on the aquatic environment (Heathwaite *et al.*, 2005b).

2.2.1 Diffuse pollution

Diffuse pollution affects both surface waters and groundwater (Environment Agency, 2006) and has recently become more of an issue than point source pollution (Baker, 2003). The pollution itself is sourced 'from air, land surface, and subsurface zones and from the drainage system' (Novotny, 2003: 107). They are typically nutrients sourced from fertiliser application and enter the watercourse via leaching and/or in surface runoff (Hooda *et al.*, 2000). Thus, agriculture is globally considered to be a major source of diffuse nutrient pollutants such as nitrate and phosphorus (Heathwaite *et al.*, 2005b). Diffuse pollution is more difficult to monitor and manage than point source pollution. One reason for this is because point sources operate continuously and are more concentrated, whereas diffuse sources are more episodic in nature and can be associated with high discharge events (Edwards and Withers, 2008). Secondly, catchment characteristics and dynamics complicate management due to differences in 'soil type, climate, topography, hydrology, land use and land management' that form 'widespread, intermittent, and poorly defined contaminant sources that degrade water quality in a way that makes their control difficult' (Heathwaite *et al.*, 2005b: 446). Diffuse sources are primarily of interest in the Esk catchment due to the presence of agricultural activity. Whether by diffuse pollution or point source pollution, water quality changes within two broad spectrums: time and space. The following sections look at the evidence of spatial and temporal patterns of water quality.

2.2.2 Spatial patterns

Spatial changes in water quality reflect and are driven by catchment characteristics such as geology, climate, topography, connectivity, and human impact/land use (Drever, 1982). For example, at a simplified level, variations within a catchment's vegetation (in particular riparian vegetation) can influence the water quality. The growth of terrestrial vegetation and the method by which plant tissue is decomposed in soil directly affects the concentration of organic carbon and nitrogen-based compounds found in river water. Similarly, aquatic vegetation influences riverine dissolved oxygen, pH and phosphorus compounds (Meybeck *et al.*, 1996). Geology has a comparable influence on water quality, for example varying composition and solubility of bedrock can exert control upon the chemical properties within the soil and thus the water itself. Hem (1985) provides a thorough overview of the properties of water quality and their origins whether they are linked to climate, vegetation, geology or other catchment characteristics.

Despite natural influences over spatial trends in water quality, it is also impacted via anthropogenic factors (Baker, 2003). Humans can maintain a significant element of control upon a catchment; modifications can impact watershed hydrology which in turn transmits alterations of 'in-stream bio-geochemical processes that drive oxygen, nutrient, and sediment cycling' and thus river water quality (Chang, 2008:3285). Pollution of the riverine landscape is a growing issue and the increased emphasis upon diffuse pollution (e.g. Baker, 2003; Heathwaite *et al.*, 2005b) is changing the way we view the spatial nature of water quality.

There are a number of activities within the Esk that could be primary causes of diffuse pollution sources. Widespread activities such as managed burning, grazing of livestock and some arable farming could change the hydrological, geochemical and biological aspects of the catchment and therefore contribute towards diffuse pollution in the Esk basin. However, work must proceed with caution because monitoring diffuse pollution is difficult as this type of pollution 'varies widely as a complex function of soil type, climate, topography, hydrology, land use and land management'

(Heathwaite *et al.* 2005:446) yet it must not be ignored particularly because it must be addressed to comply with the EC Water Framework Directive (2000/60/EC).

Nitrogen (N) and phosphorus (P) are key nutrients that can pollute freshwater rivers. N and P have differing hydrological and compositional characteristics that influence their overall potential to affect the environment (Edwards and Withers, 2008). To add to this complication, Beven *et al.* (2005) have highlighted the complications and uncertainty formed by the different rates of mobilisation of nutrients thus making this a difficult aspect to quantify. Therefore, the composition of sub-catchments can influence the water quality locally; there can be spatial variability of these nutrients (and others) which needs to be taken into account. For example, Page *et al* (2005) demonstrate that soil P has hot spots, e.g. where animals graze, so within-field variability can be as high as between-field variability. Neal *et al.* (2005) have postulated that if point sources are reduced, nutrient fluxes can be reduced at a catchment scale whereas on the other hand water quality can be improved in a single tributary if diffuse sources are decreased. Therefore, which type of pollution should be our priority to reduce: both? Much of the current evidence (and legislation) seems to indicate that diffuse pollution should be (and has become) the target to tackle and thus it forms the central pollution issue engaged with in this work.

As heterogeneity is a characteristic encapsulated within natural systems, there are typically spatial variations in rates and reactions of biogeochemical processes (McClain *et al.*, 2003). As these processes can vary in space they can generate what McClain *et al.* (2003) term "hot spots". McClain *et al.* (2003: 301) define hot spots to be 'patches that show disproportionately high reaction rates relative to the surrounding matrix'. Due to differences in catchment characteristics, it is to be expected that hot spots of biogeochemical activity can be identified. It appears that hot spots can particularly be expected in riparian zones (Vidon *et al.*, 2010).

2.2.3 Temporal patterns

Water quality can also exhibit variance over a wide range of timescales. It can display trends on small scales; for example, via pollution events or storm events in a catchment. On a larger scale, the interaction of some of the factors mentioned above creates a system whereby 'concentrations of many chemicals in river water are liable to change from season to season' (Meybeck *et al.* 1996:25). At even longer timescales, changes in climate can influence water quality; however, it can be difficult to filter out 'noise' from data records to attain a true representation of this. Osborn and Hulme (2002) predict wetter winters and drier summers to be common in the UK; this trend will change the temporal trends in water quality found in UK rivers.

Land use can also change over time which influences water quality, this is discussed in depth below.

In the context of the North York Moors, the majority of the land use within the Esk catchment is managed moorland. The presence of grips within the landscape artificially drains these uplands and managed burning and grazing livestock keep the vegetation at a suitable level for the shooting practices of tourists. Ramchunder *et al*. (2009:49) note that it has long been known that 'local habitats and ecological diversity are strongly influenced by these practices'. The same authors investigate the implication of these practices (including drain blocking) upon UK peatlands. Therefore, it is fair to assume that the peat areas within the Esk catchment where burning and drainage occur, can be subjected to 'altered runoff regimes, oxidation of organic matter, changes in carbon, nitrogen and phosphorus cycling, and increased metal and suspended sediment concentrations in streams relative to intact peatlands' (Ramchunder *et al.* 2009:49). All of these effects of anthropogenic interactions upon peatlands will have direct, or indirect, consequences for the water quality and therefore upon the ecology (including freshwater pearl mussels) within the Esk itself. These consequences will vary in time and thus the impact of water quality on the habitat quality for the pearl mussel can fluctuate.

In light of the discussion of 'hot spots' above, it should be noted that temporal variations in biogeochemical processes also exist, known as 'hot moments' (McClain *et al.*, 2003). Hot moments are defined as 'short periods of time that exhibit disproportionately high reaction rates relative to longer intervening time periods' (McClain *et al.*, 2003: 301). They are dependent on the reactivation of episodic hydrological flowpaths and the mobilisation of accumulated material. It should be observed that these phenomena (both hot spots and hot moments) are solute specific; for example one riparian zone may be a hot location for nitrate but not potassium.

Finally, one principle that has been highlighted as a paradox within catchment hydrology and geochemistry that impacts on temporal water quality patterns is that of 'old' and 'new' water (Kirchner, 2003). This notion infers that in high-rainfall periods mostly old water that has been resident in the catchment is received in the channel network rather than new water from precipitation. Secondly, it appears that 'old' water has variable chemistry linked to the flow regime (Kirchner, 2003). These paradoxes in water classification ('old' or 'new') will be important to bear in mind when looking at results from high rainfall events in particular.

2.2.4 Drivers of water quality

Water quality patterns are a product of the environment they are located in. Thus the catchment environment, and in some cases the immediate locality, can drive the resulting water quality. Whilst there is a range of controls on water quality, three key drivers that are commonly highlighted in existing research are: a) catchment area; b) land use and c) connectivity. These factors will be dealt with in turn below.

a. Catchment area

Catchment area, although arguably not a driver per se, is often identified as important in field research. Burt and Pinay (2005) investigated the linkages between catchment hydrology and biochemistry. Catchment scale is highlighted as a complicating issue when addressing catchment water quality: between large catchments variation can be minimal whereas between small catchments variations in factors such as land use and geology are more significant often resulting in greater variation in water quality. This natural principle is unfortunate because typically management is focussed at larger catchments. Smaller-scale variations have been given less attention in past research yet evidence demonstrates that there is higher nutrient flux variability in smaller catchments than in larger catchments (Burt and Pinay, 2005) (see Figure 2.1).

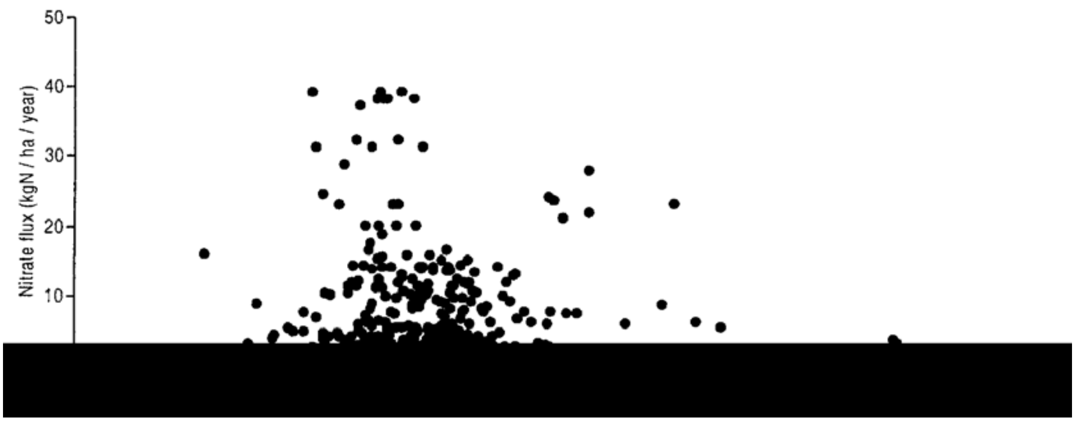


Figure 2.1: 'Relationship between drainage basin area and nitrogen fluxes in Europe and North America' (from Burt and Pinay, 2005: 298)

Therefore, the influence of drivers within the larger catchments can be hidden from analysis because of the way in which local-scale variation gets averaged out downstream. It shows that in the smaller catchments drivers can have a more direct impact upon the in-stream water quality than in larger catchments where perhaps the hot-spot signals within the catchment are lost as the impact of dilution is felt in river waters.

b. Land use

Water quality is a function of natural and anthropogenic influences that vary in time and space. Land use is a significant driver of water quality and the two elements have a complex relationship (Baker, 2003). In rural environments both diversification and intensification have created changing land uses and now such environments 'cannot be ascribed to a single land use' (Burt and Johnes, 1997: 63). A greater understanding of the relationship between water quality and land use will initiate more accurate estimates of diffuse pollution and aid water quality management in catchments that suffer with this form of pollution (Baker, 2003).

There is limited understanding of the influence of land use upon nitrate concentrations (Poor and McDonnell, 2007). Evidence has demonstrated that land use has a significant effect on the nitrogen content exported to the stream environment (e.g. Buck *et al.*, 2004; Johnson *et al.*, 1997). Due to pollution from non-point sources, nitrogen export has been correlated with agricultural land (Howarth, *et al.*, 2002); Buck *et al.* (2004) discovered that the influence of human activity upon stream nitrate was greater in agricultural areas as opposed to residential areas (during storms). Poor and McDonnell (2007) investigate how the export rate of nitrate is affected by human activity in three catchments in Oregon with similar characteristics; results from nitrate concentration sampling during storm events show that land use has a varying impact on nitrate dynamics. In agricultural areas (compared to forested and residential areas) a flushing or 'concentration' mechanism was observed in the spring and a 'dilution' pattern in autumn and winter. The 'concentration' response previously discussed by Creed *et al.* (1996) showed a N-enriched upper layer within the soil structure that is 'flushed' to the watercourse after a low-demand period enabled by the water table rising to saturate the upper soil horizons. The 'dilution' effect, observed by Webb and Walling (1985), also holds implications for the nitrate dynamics. Soil moisture levels and saturated areas expand and thus contribute a larger discharge to the river network prompting dilution of nitrate present in the catchment baseflow. Yet this process can be complicated due to delayed peaks in sub-surface stormflow as found by Burt and Arkell, (1987). It appears that these two response patterns in nitrate dynamics, dilution and concentration, can be tied to land use (Poor and McDonnell, 2007). Therefore, it will be important to assess nitrate concentrations alongside land uses within the Esk catchment to get a grip on the hot spot areas where the land use present threatens the system with potentially high nitrate concentrations.

c. Connectivity

It is also important to mention the concept of hydrological connectivity; Bracken and Croke define this as 'the passage of water from one part of the landscape to another' (2007:1749). Central to this concept lies the interaction of the landscape with the river network and thus how 'connected' a unit of land is to the river and its ability to transfer, in this case nutrients in water, from source to river. However, as connectivity is influenced by natural factors such as topographic constraints and vegetation, the complex interplay of factors makes it difficult to assess its control upon a catchment. Bracken and Croke (2007) explore connectivity in relation to the variation in space of vegetation, emphasising the complex spatial (and temporal) trends in connectivity at small scales. The presence (or absence) and spatial distribution of biogeochemical 'hot-spots' and/or pollution point sources, especially in the near-stream/river zones (Burt and Pinay, 2005), can influence the water quality and change its composition in space. Secondly, as the movement of water through a system is governed by the interaction of climate, hillslope runoff potential, landscape position, delivery pathway and lateral buffering (Bracken and Croke, 2007), variation in these components (in time and space) at a catchment scale is both dynamic and complex and needs to be carefully considered in the context of this work in the Esk.

Stieglitz *et al.* (2003) found that only periodic connection occurred, within a selection of catchments in North America, with draining water typically being spatially isolated. It was found that only when antecedent soils conditions were adequate to initiate connection in the catchment that transports nutrients to the channel. Evidence from work in snowmelt conditions in Idaho found correlation between modelling and empirical results. Ocampo *et al.* (2006: 643) discovered that rainfall events triggered varying responses from upland and riparian zones that were a) independent from one another and b) different to one another. Secondly, the evidence illustrated that typically these two distinguishable zones can be disconnected for the majority of an annual cycle. Interestingly, Ocampo *et al.* (2006) highlight that hydrological connectivity is an important concept to relate to the transport and export of nitrate which is of particular relevance here.

More recent work has developed this emergent concept further. Ali and Roy (2009) support the assessment of soil moisture and topography for the process yet highlight that a lack of consensus remains in the search for a single definition of hydrological connectivity. The following statement is presented as an attempt to derive a definition suitable to frame connectivity enquiry: 'hydrologic connectivity is a continuum of hydrological states characterised by an increased contribution from lateral subsurface water flow that sporadically activates the topographic linkages between riparian and upland areas and thus gives rise to highly correlated spatial patterns of hydrologic state variables (e.g. soil moisture) at the hillslope and the catchment scales' (Ali and Roy, 2009: 368). The authors identify landscape features, soil moisture patterns and subsurface flow pathways as key characteristics to monitor and understand when addressing the concept. Ali and Roy state that 'emergent processes like connectivity should be examined at a scale where all system components, active/inactive, connected/disconnected/unconnected, are represented' (2009: 369); therefore it is vital to address the whole catchment in light of this continuum-like process particularly when focussing spatial (and to some extent temporal) water quality patterns that are influenced by connectivity.

2.3 Management

Rivers, as an ecosystem, have been modified and interfered with at a number of levels. This has developed a requirement for effective management with the ultimate aim to effectively preserve rivers in their natural state (Boon, 1992). Diffuse pollution is a difficult problem to manage due to the spatial distribution of the problem and the spatial heterogeneity of affected areas. This is tied to the lack of understanding surrounding nutrient loss, mobilisation, and transport (Heathwaite *et al.*, 2005b). Yet the problem cannot be ignored as diffuse pollution needs to be tackled in line with the requirements of current EU legalisation (e.g. Environment Agency, 2006). It is helpful to discuss management of river catchment in two domains, the management expectations and the management mechanisms. As diffuse pollution is the primary focus in this work, it will be central to the aspects covered.

2.3.1 Expectations

There are a number of management expectations that have been enforced to restore the quality of rivers to natural or near-natural state:

- **The Water Framework Directive (WFD- 2000/60/EC)**

The WFD is a European-wide piece of legalisation as a response to degradation of aquatic ecosystems (Carstensen, 2007). This is a significant piece of legislation agreed on in 2000 and was the result of 12-year long policy process (Kallis and Butler, 2001). It aims, by 2015, to return waters (fresh, estuaries, coastal and ground) to good ecological and chemical status (Environment Agency, 2006). It is an ambitious goal with an overarching framework approach and is revolutionary with its blend of natural sciences and social elements (Steyaert and Ollivier, 2007). An interesting approach is that it leaves the translation of aims and objectives of the legislation to member states and local levels (Kallis and Butler, 2001).

There are a number of issues with the legislation that have been discussed in the literature. Firstly, there is an air of subjectivity to the WFD (Moss, 2008). For example, rivers are graded, in some cases, as 'good' which is defined as being 'slightly' below high. The grading seems to be up to the interpretation of the relevant governing bodies which could cause necessary complications. Also in that light, there is confusion of certain terms such as "ecological quality" (Moss, 2008). Allan *et al.* (2006) highlight that the WFD should be adaptable to new technologies that enhance its implementation; this must be combined with effective management and thorough understanding of the determinants monitored in the field. Secondly, to promote sustainable and harmonious monitoring in Europe, quality assurance structures should be devised to allow comparability of monitored elements (Allan *et al.*, 2006). Moss (2008) holds the view that the ability of the WFD to solve the problems posed by climate change and ecosystem degradation has already been compromised. The point argued is that 'political compromises, through the conservatism of water management bodies that have been unable to change their approach from practices that the Directive was intended to displace' have interrupted the positive advances made with the development of the legislation (Moss, 2008: 33). The conservatism has been nurtured by both contradictions and lack of definition that have been over-exploited by organisations which is not to the benefit of the WFD and its aims. The WFD must remain flexible to the issues created by climate change which has the potential to and is making schemes invalid (Noges *et al.*, 2007). Yet finally, for all the problems associated with this large-scale piece of legislation, the WFD remains the primary driver to see clean waters in UK and European rivers and surface waters and so should be strived towards when looking at the Esk situation.

- **Biodiversity Action Plan**

The Biodiversity Action Plan (BAP) was initiated by the Rio Convention on Biological Diversity in June 1992. Following this the UK BAP was devised and launched in 1994. This strategy has a species focus addressing priority species whilst aiming to see ecosystem services maintained. An improved habitat will hold both benefits for target species and ecosystem services, as summarised by Figure 2.2. The UK BAP covers 65 habitats and 1150 species (UK Biodiversity Action Plan, 2010), one of which is *Margaritifera margaritifera* (freshwater pearl mussels), the focus of this work, which is justified as the species is classed as vulnerable on the IUCN Red List.

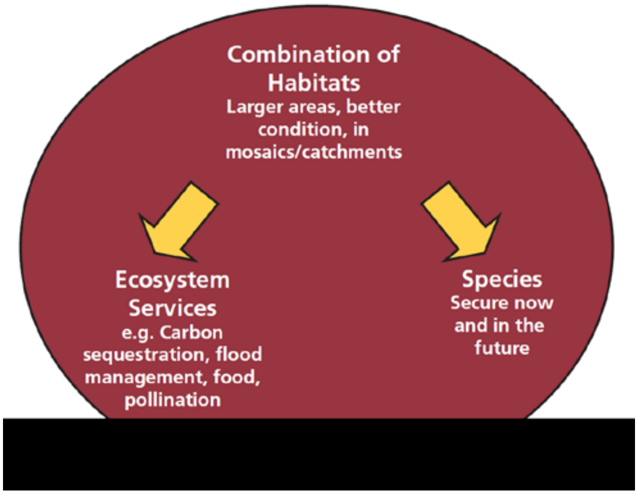


Figure 2.2: Diagram to illustrate the central purpose of the UK BAP (from DEFRA, 2007)

2.3.2 Mechanisms

To achieve the expectations discussed above there are a number of mechanisms that can be operated to strive to meet the requirements set; a number are overviewed here. Cuttle *et al.* (2007) provide an inventory of over forty methods that can be employed to control diffuse pollution that is sourced from agricultural grounds. Methods are grouped and classified within five different categories: land use; soil management; livestock management; fertiliser management; manure management; and farm infrastructure. Some methods will be more applicable than others to any specific catchment and catchment managers need to have a broad knowledge of the management options to be able to conduct an assessment of what is most applicable and estimate which will be the most effective. Buffer zones in the riparian region have been focussed on as a well known mechanism to improve in-stream water quality (e.g. Correll, 1997). Uusi-Kämppä and Ylaranta (1992) do note that buffer zones require regular harvesting to decrease the amount of stored phosphorus and nitrate within the buffers and to minimise the chance of leaching of these nutrients outside of the growing season when surface runoff can be expected to be higher. Therefore, it is important that buffers should be maintained and managed beyond their initial installation.

Vidon *et al*. (2010) highlight a number of riparian management mechanisms that can be implemented upon identification of hot spot regions. These include denitrifying walls of organic material that aids the denitrification process; reactive barriers and vegetation buffers. Riparian buffer zones are a well documented technique to reduce the removal of nitrate and organic matter to the river network. Vidon *et al.* (2010) also draw attention to the planting of vegetation that creates structure within the riparian environment that will reduce sediment mobilisation, promote infiltration and increase surface area and contact times to varying degrees of success dependent on the species. Stream fencing can also be a valuable mechanism to reduce livestock poaching of the riverbanks (Cuttle *et al.*, 2007) and to protect recovering riparian zones from damage (Vidon *et al.*, 2010). Dosskey *et al.* (2010) highlight the importance of riparian vegetation due to its positive impact on in-stream water quality, particularly diffuse pollution. Whilst scientists remain unsure how the selection of vegetation type can have impact upon the water quality there are a number of principles by which it is known to improve the water quality such as the use of large wood for channel stabilisation and nutrient adsorption by species that grow quickly. Dosskey *et al.* (2010) do raise the concern that, although it is well-acknowledged that vegetation in the riparian zones does have a positive effect on in-stream water quality, the extent to which in-stream water quality can be managed by vegetation still requires further clarification.

Finally, the Department for Environment, Food and Rural Affairs (DEFRA) have initiated land management projects such as the Catchment Sensitive Farming Programme (CSFP) that aims to maintain diffuse pollution at a level appropriate for the ecology, the catchment and its uses (DEFRA, 2002). Secondly, Natural England programmes such as Entry Level Stewardship (ELS) and Higher Level Stewardship (HLS) are strategic management mechanisms that have been implemented to aid the targets set by the expectations discussed in section 2.4.1. They are aim to provide farmers with financial incentives to manage and adapt their use of the land to aid the goals set by legislation such as the WFD. Institutional arrangement is an important aspect to consider here; whereby does the organisation and cross-body communication help the goals to be reached or not?

2.4 Freshwater pearl mussels

This study is conducted with reference to the freshwater pearl mussel (*Margaritifera margaritifera*), a long-lived river-dwelling invertebrate (lifespan periods can be over 100 years (Bauer, 1992)). Freshwater pearl mussels are viewed among the 'most critically threatened freshwater bivalves worldwide' (Geist, 2010: 69) and are listed on the IUCN Invertebrate Red List and under annexes II and V of the EU Habitats and Species Directive (92/43/EEC, 1992) and Appendix III of the Bern Convention (1979) (Skinner *et al.*, 2003; Moorkens, 2000). Its global population has significantly fallen in the past years and is now either under threat of extinction or is extremely vulnerable (Buddensiek, 1995; Cosgrove *et al.* 2000). For example, in Central Europe the pearl mussel population has decreased by 90% in the last century alone (Bauer, 1988). This is due to a combination of factors that fall into the categories of freshwater biodiversity threats that Dudgeon *et al.* (2005) postulate (see Chapter 1.0); the most important appears to be habitat degradation (Altaba, 1990), along with pollution and overexploitation (i.e. pearl fishing) (Cosgrove and Hastie, 2001). For example, Bauer (1986) found that eutrophication was the probable reason for the decline of the species south of its European range.

In Britain, the freshwater pearl mussel has been exploited since Roman times (Skinner *et al.* 2003; Young and Williams, 1983). Thankfully, for the species, the activity of pearl fishing is now outlawed and the species has been granted legal protection since 1998 (Skinner *et al.*, 2003). It used to be common in UK rivers yet this is no longer the case and it is estimated that pearl mussels survive in around 105 rivers in the UK; the majority of which are in Scotland with only 10 populations remaining in England, where even the most healthy population has few juveniles and displays evidence for decline in numbers (Geist, 2010). Skinner *et al.* (2003) and Bauer (1988) postulate that the decline in the past was undoubtedly the pearl fishing industry; however, the recruitment (the development of juvenile to adult mussels) problem currently plaguing the remaining populations is related to pollution and siltation.

2.4.1 Pearl mussels and water quality

Pearl mussels have a life cycle that consists of four individual stages (Bauer, 1988). An adult phase when it survives as a filter feeder; the glochidial phase (the pre-host attachment period); a parasitic phase, when the encysted glochidia rests on the gills of host fish; and the juvenile phase (first 20 years of the lifespan), when the species is buried in substrate and then survives living interstitially in the sediment (Bauer, 1988; Skinner *et al.* 2003). Hastie *et al.* (2000a) found that the juveniles' habitat preferences are not as wide as those of adults. Therefore, a complication of the interaction between freshwater pearl mussels and water chemistry is how the quality impacts the different stages of the species. It appears from research conducted that water quality has been a significant element to the decline in pearl mussels currently experienced (Bauer, 1988).

Water quality has received much attention in the literature and it is still unknown what requirements best support the species (Skinner *et al*. 2003). Bauer (1988) states that pearl mussels prefer oligotrophic conditions – poor in nutrients, pH of 7.5 or less and low conductivity. However, to be critical, Bauer's work was based on presence/absence within rivers in Central Europe; therefore many differences exist such as climate, land use, geology, all which influence the water quality of an ecosystem. Moorkens' (2000) study in Ireland indicates that low levels of nutrients must be required to support the species and the salmonids that support the pearl mussel whilst in their parasitic phase and Bauer (1988) notes that enrichment of the natural river systems are unfavourable to the pearl mussel. Therefore, this evidence disagrees with the controversial study (Moorkens cites Hrusca, 1995) that suggests that mildly eutrophic water promotes the survival of the pearl mussel. Moorkens (2000:4) found that at the sites studied ‘significant associations between mussel rivers and ... low conductivity, pH, oxidised nitrogen and BOD values’ were displayed. This study also indicated that pearl mussel populations prefer lower levels of orthophosphate. Similarly, Buddensiek (1995) investigated how the water quality in a number of rivers in the Luneburg Heathlands (Germany) affected pearl mussel cultures located within the watercourses. In most cases a negative correlation was discovered between growth/ survival and the following parameters: conductivity, ammonia, nitrate, phosphate, sodium, potassium, calcium and magnesium. These chemical variables are all indicators of eutrophication and thus this research substantiates the claim that nutrient enrichment has an adverse effect upon freshwater pearl mussel populations.

Studies have sought to determine the minimum water quality standards for the freshwater pearl mussel (e.g. Buddensiek, 1995); however, the ability to estimate these levels is an issue as the species is declining globally reducing the viable study areas. Thus, to investigate water quality at high resolution in a catchment where a remaining pearl mussel population still survives is an important focus to begin to highlight how spatial and temporal variations can influence the species.

2.4.2 Case study: Pearl mussels in the River Esk

This study focuses on the water quality within the River Esk, located in the North York Moors National Park. In 2006, the Esk Pearl Mussel and Salmon Recovery Project (EPMSRP) was initiated to aid the conservation of the species. Evidence of decline of the freshwater pearl mussel population in the River Esk was recorded by Natural England (NE) and Environment Agency (EA) commissioned surveys conducted in 1995 and 1999 (Oliver and Killeen, 1996; Killeen, 1999). The mussels recorded during the surveys were all large and elderly suggesting that recruitment has not taken place for several decades (NYMNPA Freshwater Pearl Mussel Species Action Plan, 2008). This corresponds with the evidence of Hastie *et al.* (2000a) whereby juveniles’ habitat range is not as large as adult pearl mussels. Pearl mussels require clean, high-quality environments for their survival, promoting species recruitment. The literature has suggested that the reduction in pearl mussels may not be because of poor water quality yet it may display the requirement of very high quality of the pearl mussel (Moorkens, 2000). This concept correlates to the situation in the Esk as Bracken (2009) postulates that the water quality in the river is of high standard (meets drinking water standards) but even low levels of nutrients are capable of preventing the recruitment and survival of the pearl mussel. Therefore, as water quality is a variable of importance to their survival and places significant demands on the quality of the environment (e.g. Skinner *et al.*, 2003), research to understand the spatial and temporal trends in water quality of the Esk is vital. Indeed, consultant Ian Killeen discovered limited suitable pearl mussel habitat during site visits in winter 2009 and called for extensive water quality assessment to aid conservation aim (Killeen, 2009). This form of assessment will aid the successful re-introduction of pearl mussels to the River Esk and contribute to the conservation of the pearl mussel locally (in the Esk catchment), nationally and globally.

2.5 What are the gaps in our understanding?

In the context of this literature it appears that a significant gap in knowledge is the influence of water quality upon the freshwater pearl mussel. Indeed, Cosgrove *et al.* (2000:207) postulate that there is much still unknown about the ecology of the freshwater pearl mussel and therefore to further this understanding and conserve the species in the rivers of the UK it is 'important to identify the water quality requirements for the species, so that these form the basis of future water quality standards'. Skinner *et al* (2003:13) adds weight to this assertion stating a priority of future research is the 'effects of eutrophication (and water quality requirements, especially in England)'.

Water quality may be more crucial to the survival of the pearl mussel within the Esk than previously thought (Bracken, 2009). In the Esk it is known that the water quality is of a high standard, in many ways this may be why it has not been investigated in detail before; thus, a high-resolution study to this catchment will redress this gap in our knowledge. Before pearl mussels can be re-introduced to the Esk, more needs to be understood about the water quality and how it changes in space and time. This notion is supported by Moorkens (2000) who acknowledges that for successful conservation of the pearl mussel river quality must be addressed'.

The research undertaken in this work aims to fill the gap in knowledge regarding water quality in the Esk and is vital to determine the future survival of juvenile freshwater pearl mussels. For this to occur, a valid assessment of the water quality within the Esk is necessary to comment on the implications of the catchments water to the health and population of the pearl mussels. When results have been analysed and potential hot spots designated, management solutions can be explored.

2.6 Summary

In summary, key literature has been presented that highlights diffuse pollution as a central problem in the Esk catchment. The heterogeneity within catchments means that diffuse pollution can be more difficult to manage, yet it is a target in light of the WFD and when considering a means to address the BAP. Spatial and temporal patterns have been identified and the key drivers of water quality, namely catchment area and land use, have been discussed. Developing hydrological catchment research themes connectivity and biogeochemical hot spots and moments have been highlighted as they are expected to be of importance within this work. Finally, freshwater pearl mussels and the case study of the population within the Esk catchment are introduced that in particular emphasise the current research needs in this area.

3.0 Methodology and Sites Outline

3.1 Introduction

This chapter outlines the methods used in this study. Firstly, the background to the study catchment is provided (section 3.2) and the location of field sites are discussed and justified (section 3.3). This empirical study consisted of fieldwork (section 3.4) and laboratory (section 3.5) elements, as well as a number of analytical methods (section 3.6), which are all reviewed. The first objective, to collect and analyse spatial and temporal water quality parameters in the Esk catchment using a range of methods, is addressed by the monthly sampling strategy and high resolution sampling. The second objective, to determine the relationship between land use and catchment area with water quality in the river system, is explored using analytical methods that enable the investigation of relationships between empirical data and these catchment characteristics (section 3.4). The third objective, suggesting methods to improve the water quality to help efforts to conserve freshwater pearl mussels, is addressed indirectly by building a knowledge base of the water quality status, thus allowing management techniques to be discussed with a suitable foundation. The final objective, which considers use and value of a high-resolution dataset to illustrate the ecological status of a river basin system to map on to management expectations, was addressed indirectly by empirical understanding of the water quality levels.

3.2 The study area

3.2.1 Location and topography of the River Esk

The River Esk catchment is located in the North York Moors National Park, Northern England and drains the northern area of the Park. The Esk travels from headwater catchments in the west 42 km to the coast, draining an area of 362 km^2, directly entering the North Sea at Whitby (EA, 2005). There are a number of tributaries that generate discharge that enters the main stem, some that drain high moorland areas (headwater regions) and others that drain land downstream typically from a greater mix of moorland, improved pasture and arable land. The majority of the catchment lies to the south of the Esk with tributaries draining steep sloped moorland in southern sub-catchments to the system (EA, 2005). The Murk Esk is a notable catchment which accounts for 25% of the total drainage basin area and joins the Esk at Grosmont. The Esk upstream of Grosmont, a village located on the Esk, will be the focus of this study because this is the region where freshwater pearl mussels have been recognised and surveyed to be surviving in the river system (Oliver and Killeen, 1996; Killeen, 1999; Esk Pearl Mussel and Salmon Recovery Project, 2010b).

The headwater catchments contain areas of higher topography; the highest point in the catchment is in the south western portion of the catchment drains from a height of 434 m above sea level (see Figure 3.1). Topography links into channel morphology which varies in the Esk as it meanders gently across a 200-300 m floodplain between Castleton and Lealholm with steep valley sides either side. However this distance narrows downstream of Lealholm to around Glaisdale with more rapids and waterfalls present.

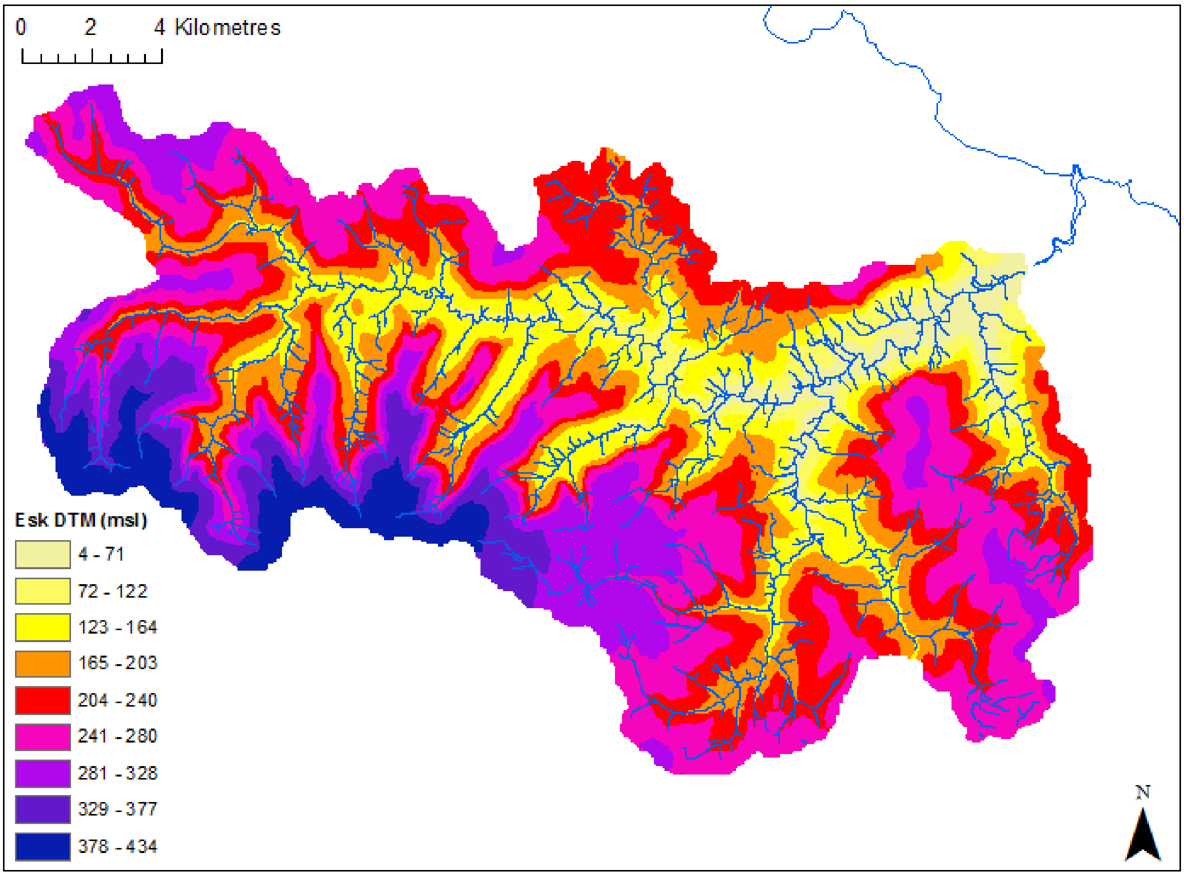


Figure 3.1: Catchment topography from Esk catchment Digital Terrain Model (DTM) (10 x 10 m resolution)

To complement the outline above it is also necessary to consider catchment geology, climate, land use and vegetation. For further information regarding these catchment characteristics see Mills (2006), EA (2005) and Carroll and Bendelow (1981).

3.2.2 Geology

Mid-Jurassic Ravenscar Group geologies dominate the Esk catchment with shale, sandstone and limestone (oolite) covering much of the area that create the high moorland regions (EA, 2005) (see Figure 3.2a). Stainforth (1993) identifies Lias shales in parts of Eskdale and the Murk Esk catchment that can be eroded and transported with greater ease. Glaciers cut the path and eroded the solid geologies to expose the weak Lias shales. Glaciers extended up valley depositing boulder clay in the region (Carroll and Bendelow, 1981) (see Figure 3.2b). Glacial activity is particularly located downstream of Lealholm influencing the river path (Bracken and Warburton, 2005). A narrow band of alluvium deposits are present within the landscape, yet the presence of this material is constricted by valley sides (EA, 2005). The EA (2005: 35) term geology to be a ‘key factor in the generation of flooding’ as the porosity of geologies and the capability to store storm water are aspects that dictate the catchment response to precipitation inputs.

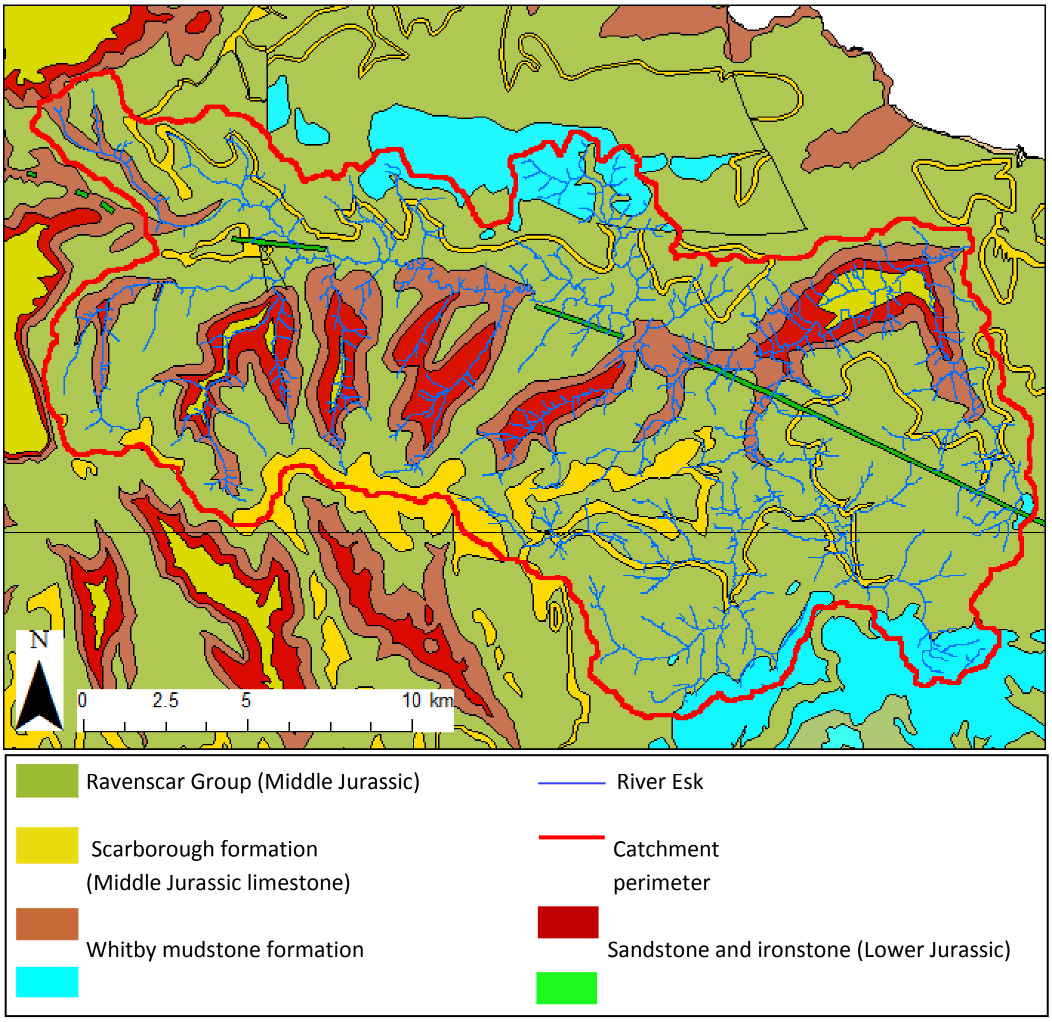


Figure 3.2a: Bedrock geologies in the Esk catchment and the surrounding region

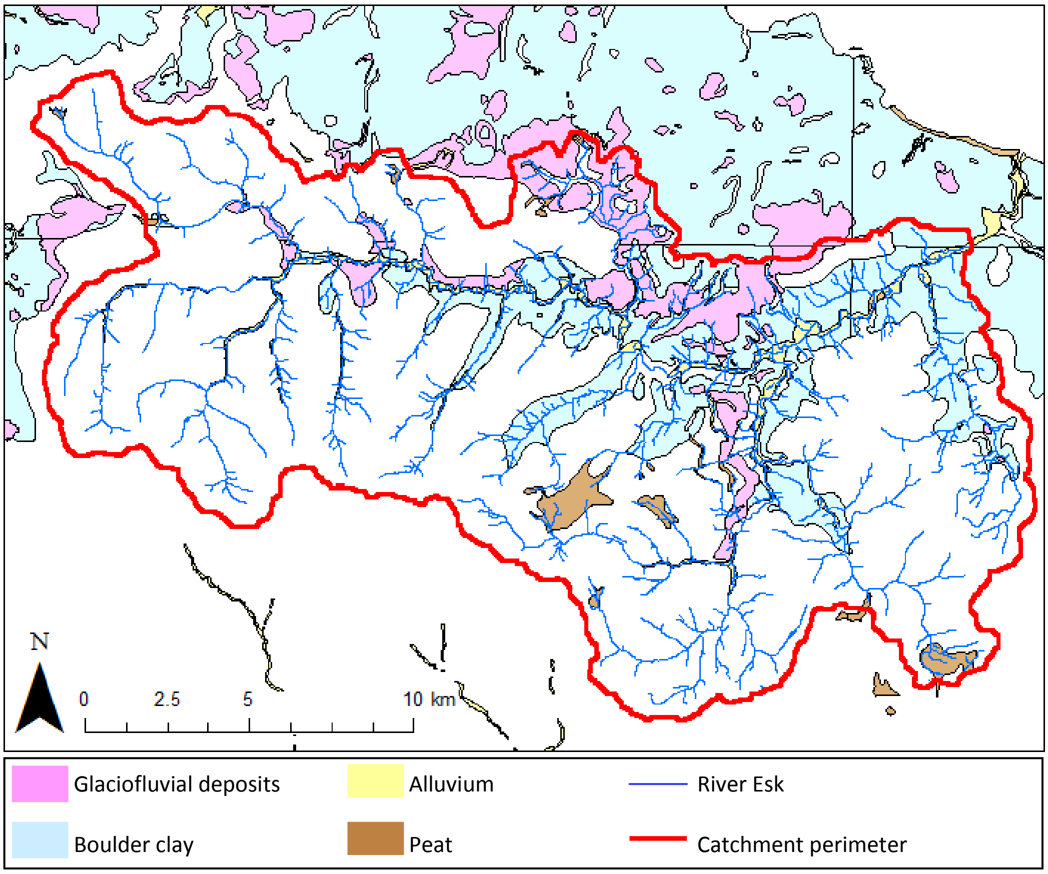


Figure 3.2b: Drift geology of the Esk catchment and the surrounding region

3.2.3 Climate

The Esk catchment has a cold and wet temperate climate (Mills, 2006). Typically mean annual precipitation ranges between 700 and 1000 mm with the highest values recorded at the highest elevations (see Figure 3.1) (www.metoffice.gov.uk; EA, 2005). Typically frontal storms deliver the majority of precipitation received by the catchment with convective storms in the summer months. Mean temperatures range from 2 °C in January to 16 °C in August (Mills, 2006); this evidence is strengthened by local weather station data located in Westerdale (upper headwater tributary) which in 2009 recorded an average temperature of 2 °C in December and 15 °C in July and August (weather.westerdale.info). It is worth noting that this study period collided with the coldest winter in the UK since 1978/79 (Met Office, 2010) with high snow falls and low temperatures persisting in the North York Moors as well as around the UK, for example the same local weather station recorded 14 cm of snow in December 2009.

3.2.4 Land use and vegetation

Land use is a key characteristic of a catchment; definitions relate to the land practices and management that occurs at a given location. It is relevant to this study as land use has an impact on water chemistry (e.g. Baker, 2003). For example, land used for arable farming will have a different influence upon the water chemistry land used for extensive grazing. Accurate land use data is extremely difficult to obtain (Foresight Landuse Futures Report, 2010). Here land cover is used as a surrogate for land use and the Centre for Ecology and Hydrology (CEH) Landcover Map (LCM) is used to gain an impression of the land use in the catchment (Figure 3.3) (for further details on the CEH LCM see section 3.6). Land cover differs from land use in that it does not include management practices and is coarser, in terms of categories. For example, the improved pasture category accounts for silage crops and permanent grazing, which will differ in terms of the volume and frequency of fertiliser application. Despite this, the CEH LCM is the best available source to gain an impression of the land use of the UK. Although this data provides a coarse representation it does capture the key distinctions in the catchment and is thus the best available surrogate for land use.

The catchment vegetation is dominated by upland heath or moorland, illustrated in Figure 3.3, where *Calluna vulgaris* (heather) is particularly present; however, grasses and bracken can also be found. These areas are carefully managed and maintained by controlled burning with both sheep grazing and grouse shooting in mind (Carroll and Bendelow, 1981). Improved pasture is located in the lowlands (Bracken and Warburton, 2005), and typically found on the floodplain of the main stem. Areas of bog are present in regions of high topography (by the watershed of the southern perimeter of the catchment area). There are a number of areas of broad leafed woodland with natural deciduous species; these areas are especially located in the river valleys. Coniferous plantations e.g. Danby High Moor, that have been established on areas of removed moorland are also located in the catchment. Urban areas can be identified within the catchment, typically situated in the valley such as Danby, Glaisdale and Grosmont. The economy of the area is based on agriculture and tourism with fishing and grouse shooting attracting visitors.

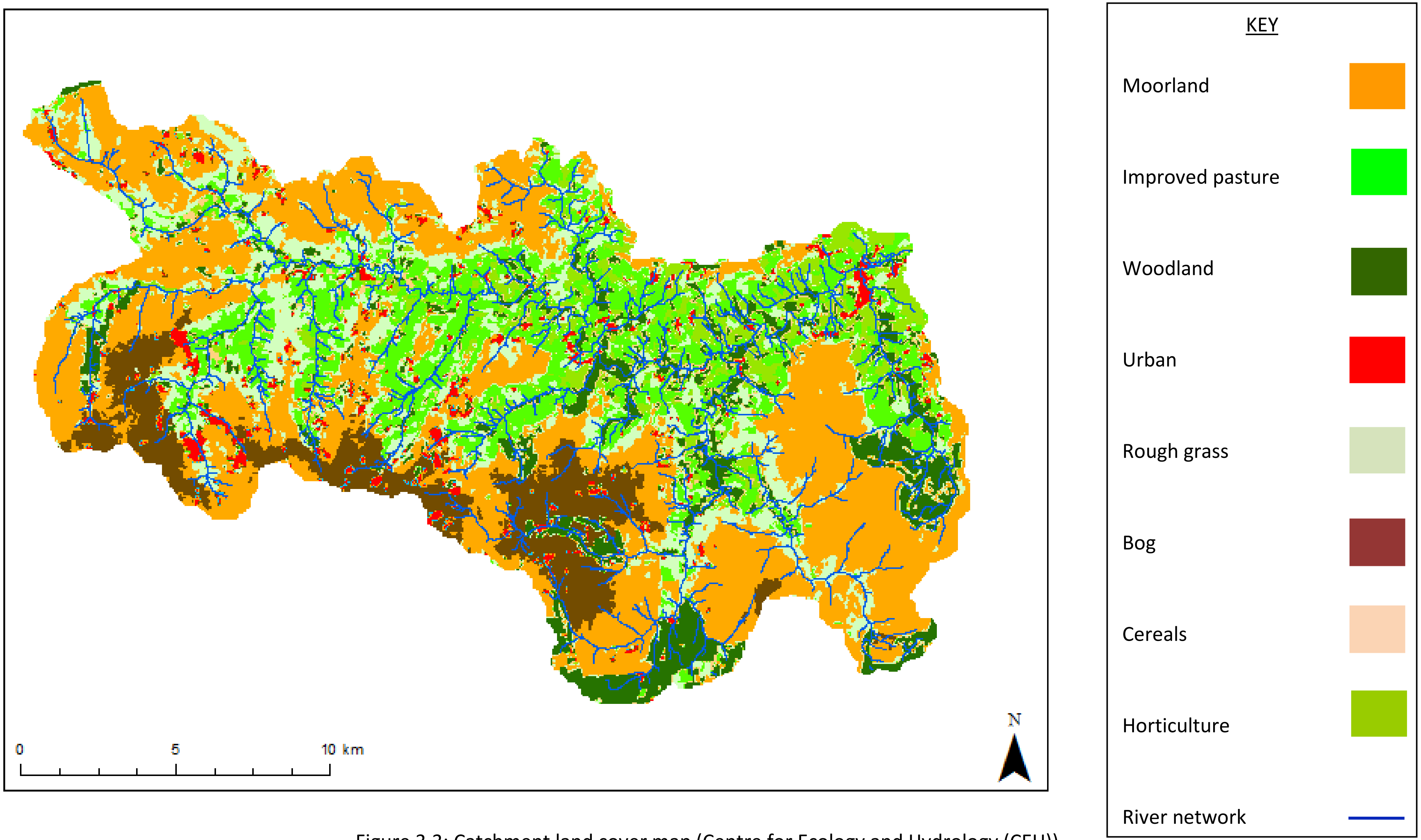


Figure 3.3: Catchment land cover map (Centre for Ecology and Hydrology (CEH))

3.3 Site locations

Monthly sampling was conducted at 20 sites in the Esk catchment (see Figure 3.4). Sites were selected to gain a wide spatial sample of river water; both headwater tributaries, in the west, and lowland tributaries downstream, in the east. Sites were also distributed regularly along the main stem as far east as Grosmont. Environment Agency assessment of species cover found the mussels between Danby and Glaisdale (NYMNPA Species Action Plan, 2008) and therefore most work was conducted upstream of Glaisdale incorporating both tributaries and reaches within the main stem. A number of sites were assessed downstream of Glaisdale to Grosmont as the pearl mussel surveys are by no means conclusive as to the spatial extent of the species distribution. Significant tributaries were selected for assessment based on their size. A significant factor within this was the distribution of pearl mussels. A number of sites were recommended by the ESPMRP Project Leader (Simon Hirst) and the distribution of sites was approved by the NPA. As a range of tributaries (and main stem sites) were sampled, there was variability in terms of the catchment area. The areas derived (for method see section 3.6) are presented in the Table 3.1.

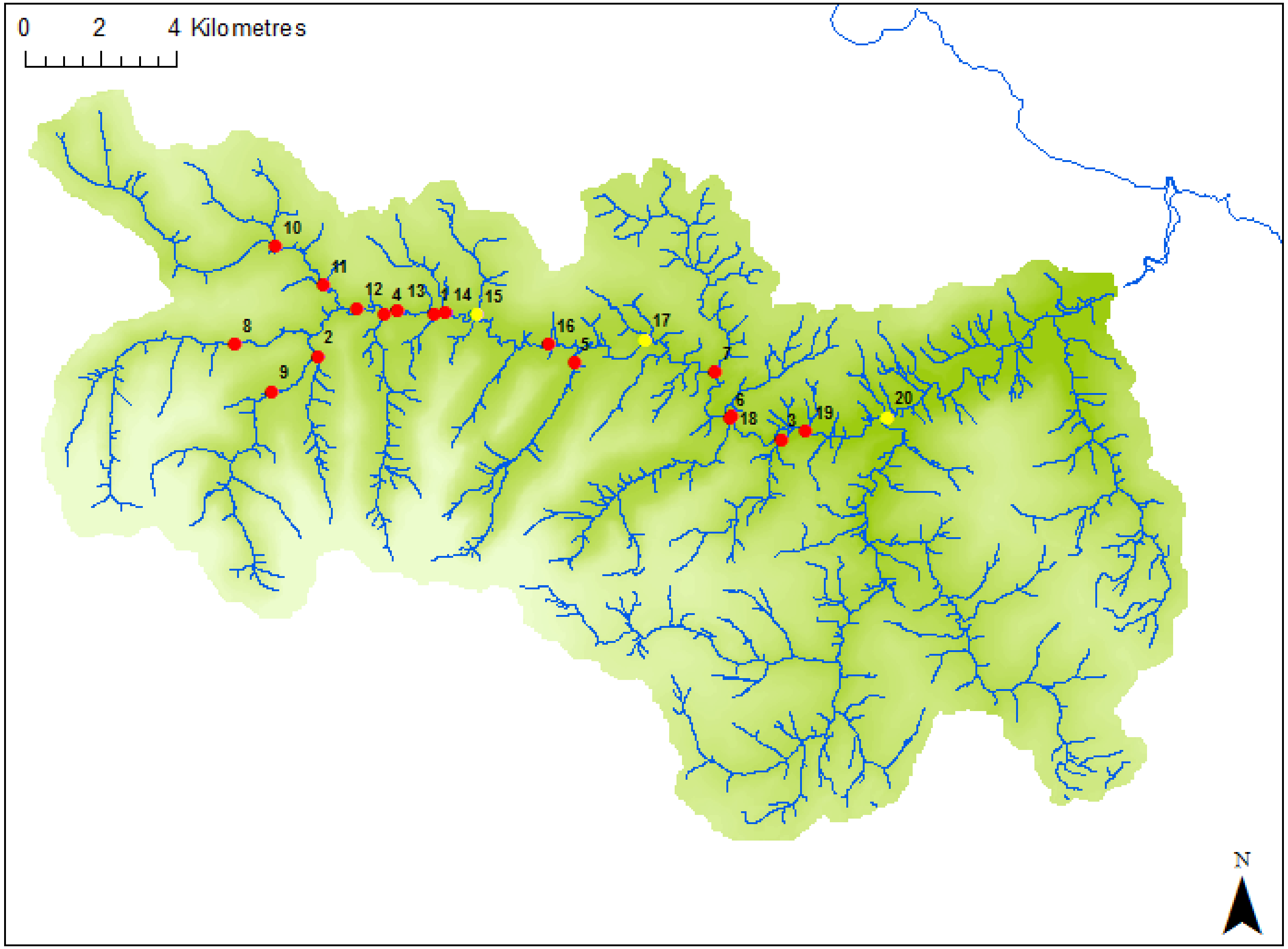
Table 3.1: Catchment areas for all sample points in the Esk catchment

SITE	**Site ID no.**	**TRIBUTARY *or* ESK MAIN STEAM**	**CATCHMENT AREA (km^2)**
Toad Beck	1	Tributary	1.8
Tower Beck	2	Tributary	6.7
Butter Beck	3	Tributary	8.8
Danby Beck	4	Tributary	12.4
Commondale Beck b	5	Tributary	13.7
Stonegate Beck	6	Tributary	13.9
Great Fryup Beck	7	Tributary	14.2
Glaisdale Beck	8	Tributary	15.4
Hob Hole	9	Tributary	17.5
Westerdale beck	10	Tributary	19.2
Commondale Beck a	11	Tributary	24.6
Esk at Castleton	12	Esk	74.6
Esk at 6 Arch Bridge	13	Esk	88.4
Esk at Danby Road Bridge	14	Esk	95.9
Esk at Danby Moors Centre	15	Esk	96.6
Esk at Houlsyke	16	Esk	110.8
Esk at Lealholm	17	Esk	129.3
Esk at Glaisdale	18	Esk	160.3
Esk at Egton Bridge	19	Esk	188.2
Esk at Grosmont	20	Esk	284.7

Sites were located close to the confluence of the tributaries with the main stem to attain an impression of the signal from the total area of the sub-catchment and also to capture a view of the levels that enter the main stem. The GPS co-ordinates were recorded using a hand-held receiver and the data inputted to ArcMap to create Figure 3.4. Similarly to Milan *et al.* (2010), sites were also selected to give a wide range of sites that had varying land cover e.g. moorland dominated (e.g. Hob Hole Beck) versus improved pasture dominated (e.g. Toad Beck); the percentages of the three main catchment land covers (arable, improved pasture and moorland) are presented in Table 3.2 below. The method of derivation for the land cover percentages is overviewed in section 3.6 (Catchment Characterisation). Another factor in site selection was ease of access to the river: where possible, sites were sampled nearby to road bridges, as suggested by Mäkelä and Meybeck (1996).

Table 3.2: Percentage of three main land cover types (arable, improved pasture and moorland)

Site	**Site ID no.**	**Arable (%)**	**Improved pasture (%)**	**Moorland (%)**
Toad Beck	1	13.6	49.2	11.7
Tower Beck	2	4.4	29.3	31.8
Butter Beck	3	4.1	19.4	40.3
Danby Beck	4	7.9	26.6	33.7
Commondale Beck (upstream)	5	3.9	6.5	69.2
Stonegate Beck	6	14.2	29.4	40.9
Great Fryup Beck	7	6.9	37.0	18.6
Glaisdale Beck	8	8.0	27.3	30.3
Hob Hole	9	2.1	3.6	62.0
Westerdale beck	10	1.9	10.3	29.8
Commondale Beck (downstream)	11	3.7	6.7	65.5
Esk at Castleton	12	2.8	10.2	50.9
Esk at 6 Arch Bridge	13	3.5	12.6	48.3
Esk at Danby Road Bridge	14	3.7	13.2	48.6
Esk at Danby Moors Centre	15	3.7	13.4	48.3
Esk at Houlsyke	16	4.8	14.9	47.6
Esk at Lealholm	17	5.5	18.3	43.4
Esk at Glaisdale	18	7.8	20.8	40.7
Esk at Egton Bridge	19	8.0	21.6	39.0
Esk at Grosmont	20	6.9	17.0	42.2



Identification Key

1: Toad Beck
2: Tower Beck
3: Butter Beck
4: Danby Beck
5: Great Fryup Beck
6: Glaisdale Beck
7: Stonegate Beck
8: Hob Hole Beck
9: Westerdale Beck
10: Commondale Beck (upstream)
11: Commondale Beck (downstream)
12: Esk at Castleton
13: Esk at 6 Arches
14: Esk at Danby Road Bridge
15: Esk at Danby Moors Centre
16: Esk at Houlskye
17: Esk at Lealholm
18: Esk at Glaisdale
19: Esk at Egton Bridge
20: Esk at Grosmont

Sample site
Sample site and automatic sampler site*
* Site 15 and 20 locations of logging stations

Figure 3.4: Location map of sample sites within the Esk catchment

3.4 Field Techniques

Field methods are divided into two components: firstly, the routine monthly sampling programme which primarily promotes an image of the spatial distribution of parameters but also allows for the assessment of change over the 8-month period. Secondly, the sampling at a higher resolution using automatic samplers, typically investigating trends over a 24-hour period.

3.4.1 Monthly monitoring system

A routine water sampling programme was conducted between October 2009 and June 2010 to gain a representative picture of water quality over the study period. A monthly resolution of samples was used to ensure seasonal variability was captured. This was completed by taking a water sample from the river using water sampling equipment whilst wearing nitrile gloves. The use of the gloves reduced the chance of contamination as they are chemically resistant. Water samples were taken from the area of most rapidly moving water that was safely in reach using the sampling equipment; this meant that in most cases water was sampled from areas with moderate flow as opposed to from pools where the flow is minimal. Samples were contained in 50 ml vials and stored in a cool bag with ice packs to ensure they remained cool to minimise levels of bacterial growth/decay during transit. Upon return from the field to Durham, samples were stored in a laboratory fridge until analysed.

A YSI multi-parameter probe was used to measure pH, dissolved oxygen (%) and electrical conductivity (µS/cm). The probe was calibrated in the laboratory prior to use in the field using certified calibration standards. The sensors were rinsed with deionised water in-between standards to prevent any cross-contamination. One minute was given to allow the readings to stabilise before calibrating. The work in the field with the YSI probe was conducted over a subset of the monthly sampling period (4-months) to add to the data received from the water samples and aid further catchment characterisation. The YSI lead from the hand-held computer and the protective-metal cage again allowed the river water variables to be sampled within the flow rather than slower-moving pools. The probe was left to stabilise in the water before readings were recorded.

3.4.2 High-frequency sampling

As water quality monitoring is observing a changing process with both annual fluctuations and more short-term fluctuations (Loftis and Ward, 1980), this makes it important to assess variables at a range of timescales to see how parameters are affected. The repetition in the spatial survey allowed seasonal monthly fluctuations to be assessed. Three sites in the catchment were identified for higher resolution sampling: the Esk at Danby Moors Centre, the Esk at Lealholm and the Esk at Grosmont. Danby and Grosmont were identified to be suitable in this study due to being at the approximate estimated maximum extent of the pearl mussel species habitat in the Esk. Secondly, it is interesting to investigate how the variation in hydrological activity influences water quality i.e. the Danby site presents a 'flashier' regime to that at Grosmont. The new system installed at Lealholm, with permission of the Danby Court Leet, was undertaken as this area has been highlighted to be prime habitat grounds for freshwater pearl mussels (Killeen, 2009). Each site is a location in the monthly sampling programme (see Figure 3.4). At these three sites, automatic water samplers (autosamplers) were deployed. The ISCO 6712 model was used at the Esk at Danby Moors Centre and the Esk at Lealholm and a Sigma 900 at the Esk at Grosmont. These systems allow for high frequency sampling with specified time intervals and specified volumes removed. Additionally, they can be set to sample when a stage increases above a specified height; this is done by using a float switch which triggers the system to operate. Therefore they can sample both baseflow and stormflow water quality. Samplers were programmed to remove 950 ml (for ISCO the systems) and 450 ml (for the Sigma system) (this difference is related to system capacity) at 60-minute intervals when activated. As the systems have the capacity to hold 24 sample bottles, this allowed the water quality over a 24-hour period to be monitored. The float switches were set at varying levels throughout the year to enable the equipment to capture water samples during the rising limb and peak of a storm event. The autosamplers record the time and date when the sample was removed to allow for logged data (see below) to be used in parallel. The use of automatic samplers to assess water quality at varying stage levels where stage is logged is common in other studies e.g. Riedel and Vose (2002). This allowed for a synchronous network that was left to be resident in the catchment with the potential to attain an insight into the influence of stage upon water chemistry to be established. One issue with the samplers related to the battery life, potentially limiting the number of sample bottles taken once the systems were triggered. For example, if the a battery failed after 18 samples, the final 6 hours of water would be missed; this created problems when looking at the delay in parameter signals post-storm events.

At the Esk at Danby Moors Centre and the Esk at Grosmont sites, a Campbell CR10X data logger, was used to record stage and turbidity, logging data at a 15-minute intervals. Stage was monitored using a Druck PDCR1830 pressure transducer located at the base of the stilling well. Logged stage data from Danby were corrected by 12 cm to ensure true stage levels were used during analysis; the height that the transducer was offset from the river bed was measured to calibrate for this factor. Turbidity was monitored using an Analite 390 probe alongside the respective stilling wells. Data were logged from October 2009 to July 2010.

Measuring stage accurately is essential to this work as it allows the in-stream water parameters to be assessed alongside stage to see how variables respond to changes over time. Figure 3.5 shows the stage record from Danby; the stage values presented are the daily average stage values (in metres).

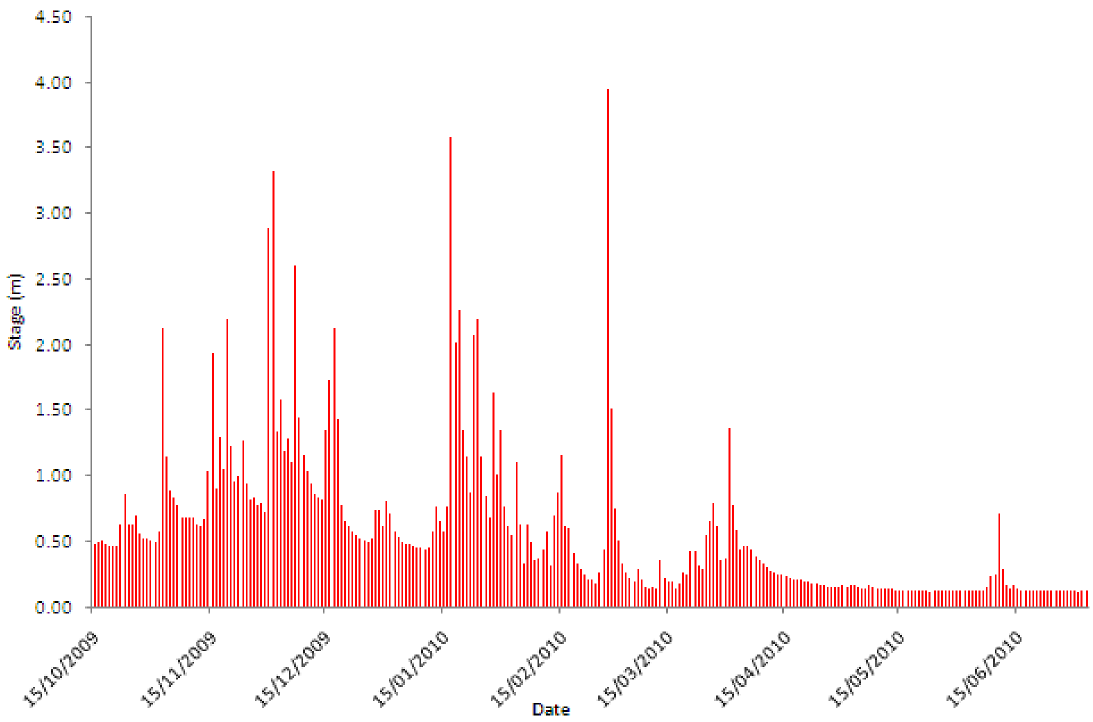


Figure 3.5: Stage record at Danby (daily average stage) from mid-October 2009-early July 2010

The Danby stage record reveals a baseflow system that is subject to flashy responses to precipitation inputs. There are several high peaks in daily average stage such as late February 2010 which records stage to be approximately 4.00 m. Conversely, the previous day the river's stage averaged a depth approximately 0.5 m, illustrating the flashy nature of the Esk at Danby. With the exception of a peak early in June 2010, since early April the stage levels indicate the system stabilises to a springtime/summertime baseflow of around 0.1-0.2 m. Similarly to other annual cycles the baseflow during the autumn and winter is higher and the frequency in stage peaks is greater.

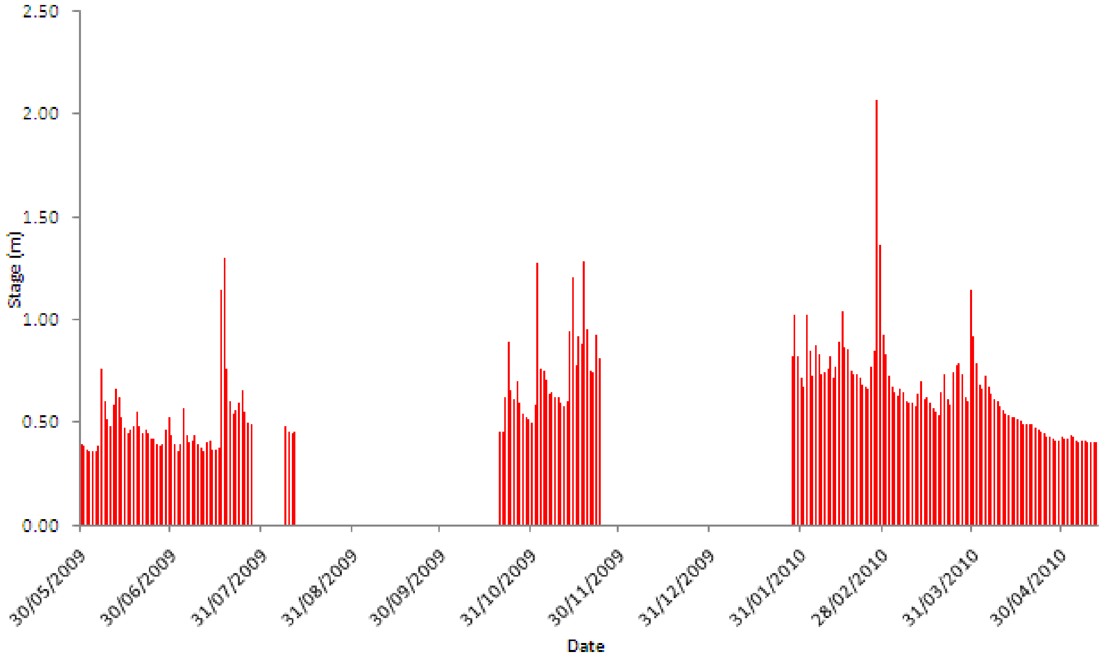


Figure 3.6: Stage record at Grosmont (daily average stage) from mid-June 2009-mid-May 2010

The Grosmont record (Figure 3.6) utilises data from outside of the monitoring period of this study logged throughout the summertime (May-September 2009). The gaps in the data record are due to battery failure where the solar panel was shaded and receiving reduced sunlight over the autumnal/winter period causing the battery to be drained. However, the record displays the baseflow level is higher than at Danby with daily average stage in June around 0.4 m for example. The record indicates how the baseflow element increases during the winter months. The stage levels do not have maximum values as large as those at Danby. Late February 2010 stands out as the largest storm peak with a stage level of approximately 2.0 m.

3.5 Laboratory Techniques

In the laboratories at Durham, work was focussed in two domains: anion and cation analysis, and suspended sediment concentration determination. The processes that the samples were subjected to are explained below.

3.5.1 Anion and cation analysis

It is important to work on samples at an immediate basis; water samples from the routine monthly sampling run were stored in a fridge to reduce bacterial activity within the sample and analysis was undertaken as soon as possible, typically the day following fieldwork. Samples were filtered, whilst wearing nitrile gloves, through a Whatman filter paper with a pore size of 0.2 µm. Bacteria are typically about 1.0 µm diameter so the majority of bacteria are removed, minimising the risk of any change in the sample chemistry, which especially affects the nitrate concentration that is of particular interest here. Typically 10 ml of the filtered water was required for Dionex preparation to allow for multiple runs should the equipment incur operation problems and re-runs be required.

The Dionex system analysed water for anions, using a DX500 operating system, and cations, using an ICS 1000 operating system. This use of ion chromatography has been widely used within the literature e.g. Ahearn *et al.* (2005); Rhodes *et al.* (2001). The equipment monitors for fluoride, chloride, nitrite (as N), bromide, sulphate (as S), nitrate (as N), phosphate (as P), sodium, ammonium (as NH_4^+), potassium and magnesium. The anion system operates a gradient programme of eluent, potassium hydroxide (12.0 mM→39.0 mM), and uses mechanical eluent generation to provide continuity in the solution. On the other hand the cation system operates an isocratic programme and requires manual eluent generation of the eluent, methane sulfonic acid (MSA). The anion system uses an AS18 column and the cation system uses a CS16 column. The column essentially provides a reactive surface that separates ions into groups of the same charge and size so the concentration in the sample can be detected in turn as they exit the column. Suppressed conductivity detection is primarily used; however, UV/VIS detection (at 210 nm) is used to remove interference for nitrate and nitrite. The detection limits provided in Table 3.3 indicate the lowest signal that can be reliably detected and approved at a 99 % confidence level. Any values that were below the detection limits were not used in any following statistical analysis and the sample record of that site/time regarded as not applicable (n.a.).

Table 3.3: Detection limits of chemical parameters (method used is suppressed conductivity detection apart from *when UV/VIS detection (at 210nm) is used)

Anion/Cation	**Detection Limit (mg l^{-1})**
Fluoride (as F)	0.01
Chloride (as Cl)	0.03
Nitrite (as N)	0.01
Bromide (as Br)	0.02
Sulphate (as S)	0.02
Nitrate (as N)	0.02
Phosphate (as P)	0.02
Nitrite (as N)	0.02*
Nitrate (as N)	0.04*
Sodium	0.05
Ammonium (as NH_4^+)	0.02
Potassium	0.01
Magnesium	0.01
Calcium	0.05

3.5.2 Suspended sediment concentration

Samples removed from the river using the automatic samplers were analysed for the suspended sediment concentration (SSC). Samples from Danby, Lealholm (950 ml) and Grosmont (450ml) were filtered using Buckner flasks and glass microfibre filter paper with a pore size of 1.2 µm. Filter papers were pre-weighed following drying in an oven (at 105 °C) and re-weighed, when moisture is removed overnight in a oven (105 °C) following filtering. This allowed the amount of sediment suspended within the sample to be derived using the following calculation:

$$\left(\left(Filter\ paper\ DRY\ weight(mg)\right) \div \left(Filter\ paper\ and\ sediment\ DRY\ weight\ (mg)\right)\right) \times sample\ volume\ (ml) = Suspended\ sediment\ concentration\ (mg\ l^{-1})$$

From the filtered water, 50 ml was decanted off into a vial for re-filtering ahead of the Dionex analysis process described above.

3.6 Catchment characterisation

A number of computational analytical methods were employed to enable the influence of catchment area and land cover measures to be investigated. Firstly, the catchment areas were calculated using a digital elevation model (10 m resolution) collected using airborne Interferrometric Synthetic Aperture Radar (IfSAR) (Figure 3.1). The data used had an elevation error of ±1 m and are available either as raw data or as a filtered Digital Terrain Model (DTM). The DTM approach was enlisted because its use reduces the complications created by both vegetation and human-made structures (e.g. settlements) (Dowman *et al.*, 2003). The catchments for each sample point were defined in SAGA-GIS (SAGA, 2010) using the “Deterministic 8” algorithm (O'Callaghan and Mark, 1984) after filling sinks utilising the Planchon and Darboux (2002) method. The area of these catchment polygons was used to calculate the upstream catchment areas for the sample points.

Secondly, the CEH LCM was used to quantify the upstream percentages of land cover types in the Esk catchment. The LCM is a digital map formed via computer analysis of satellite images typically from Landsat satellites (with a resolution of 25 m). Land cover classes were identified from the UK LCM. The data applied were in raster format (changed from the prior vector database). For each of the catchment polygons defined above the number of cells in each land cover class were counted, then divided by the total number of cells in that catchment to attain the percentage cover of that land cover in that catchment (see Table 3.2). The LCM itself identifies 16 classes and 27 sub-classes from the ‘Broad Habitats’ classification (Jackson, 2000). These classes have been divided into habitat classes of similar type: improved pasture, rough grass, moorland, bog, urban, cereals, horticulture, non-rotational horticulture, woodland and other using the classification of Milledge *et al*. (in press). The relationship between these classes and the broad habitat classes can be found in Table 3.4.

This work concentrates on the three main land cover types, which also contain some of the most problematic land covers for water quality: moorland, improved pasture and arable. Moorland areas have significant proportions of heather and have sheep freely grazing. Improved pasture areas are dominated by intensive agricultural activities such as grazing livestock or fertiliser application. To derive the arable land cover, cereals, horticulture and non-rotational horticulture were grouped together including land producing crops such as wheat, barley, vegetables, oilseed rape, and orchards (Jackson, 2000), see Table 3.4 for a full list of land covers in each classification category. This process resulted in the upstream percentages displayed in Table 3.2.

Table 3.4: CEH Land Cover Map 2000 classes and their translation to SCIMAP classes (modified from Milledge *et al*., in press)

Landcover type	**Description**	**Landcover Class**
Broad-leaved woodland	deciduous, mixed, open birch, scrub	Woodland
Coniferous woodland	conifers, felled, new plantation	Woodland
Arable cereals	barley, maize, oats, wheat, cereal (spring), cereal (winter),	Cereals
Arable horticulture	arable bare ground, carrots, field beans, horticulture, linseed, potatoes, peas, oilseed rape, sugar beet, mustard, non-cereal (spring), unknown	Horticulture
Non-rotational horticulture	orchard, arable grass (ley), set aside (bare), set aside (undifferentiated)	Non Rotational Horticulture
Improved grassland	intensive, grass (hay/ silage cut), grazing marsh	Improved Pasture
Setaside grass	grass set aside	Rough Grassland
Neutral grass	rough grass (unmanaged), grass (neutral / unimproved)	Rough Grassland
Calcareous grass	calcareous (managed), calcareous (rough)	Rough Grassland
Acid grass	acid, acid (rough), acid with Juncus, acid with *Nardus/Festuca/Molinia*	Rough Grassland
Bracken	Bracken	Rough Grassland
Dwarf shrub heath	dense ericaceous, gorse	Moorland
Open dwarf shrub heath	ericaceous, gorse	Moorland
Fen, marsh, swamp	swamp, fen/marsh, fen willow	Bog
Bog	bog: shrub, grass/shrub, undifferentiated (all on deep peat)	Bog
Water (inland)	water (inland)	NA
Montane habitats	Montane	Moorland
Inland Bare Ground	despoiled, semi-natural	NA
Suburban/rural developed	suburban/rural developed	Urban
Continuous Urban	urban residential/commercial, urban industrial	Urban
Supra-littoral rock	Rock	NA
Supra-littoral sediment	shingle, shingle (vegetated), dune, dune shrubs	NA
Littoral rock	rock, rock with algae	NA
Littoral sediment	mud, sand, sand/mud with algae	NA
Saltmarsh	saltmarsh, saltmarsh (grazed)	NA
Sea / Estuary	Sea	NA

In addition the Sensitive Catchment Integrated Modelling Analysis Platform (SCIMAP), a hydrological model developed by Lane *et al.* (2006) and Reaney *et al.* (2011) has been used in

Chapter 6 to validate this work and build on analysis in earlier chapters. A more complete description of the SCIMAP model can be found in Lane *et al.* (2006) and Reaney *et al.* (2011), a brief description of its key components is given here. Figure 3.7 provides an overview of the how SCIMAP outputs are built. SCIMAP uses an inverse modelling technique (Lane, 2008) to estimate the risk weighting (high risk of 1 to low risk of 0) that needs to be assigned to each land cover to optimise model performance (Reaney *et al*., 2011). The land covers are gathered from the Centre of Ecology and Ecology (CEH) land cover map (Figure 3.3) and are converged and grouped into the land classes shown in Table 3.4. SCIMAP operates by combining the 'risk' that a nutrient can be mobilised and transported via either suspension or solution and the risk of that nutrient then be delivered to the catchments channel network (the connectivity index; Lane *et al*., 2004; Reaney *et al*., 2011). When the risk at a particular point in the catchment is known, it can be transported through the system via catchment flow paths. Finally, a stretch of the river is given a relative risk (at a specific point in the river network) and this can be compared with observed nutrient concentrations (Reaney *et al.,* 2011). This comparison between the predicted risk and observed concentration can be used to infer the risk weighting that needs to be assigned to each land cover in order to maximise the strength of the relationship between the observed nutrient concentrations and modelled risks at each sample site (Reaney *et al*., 2011).

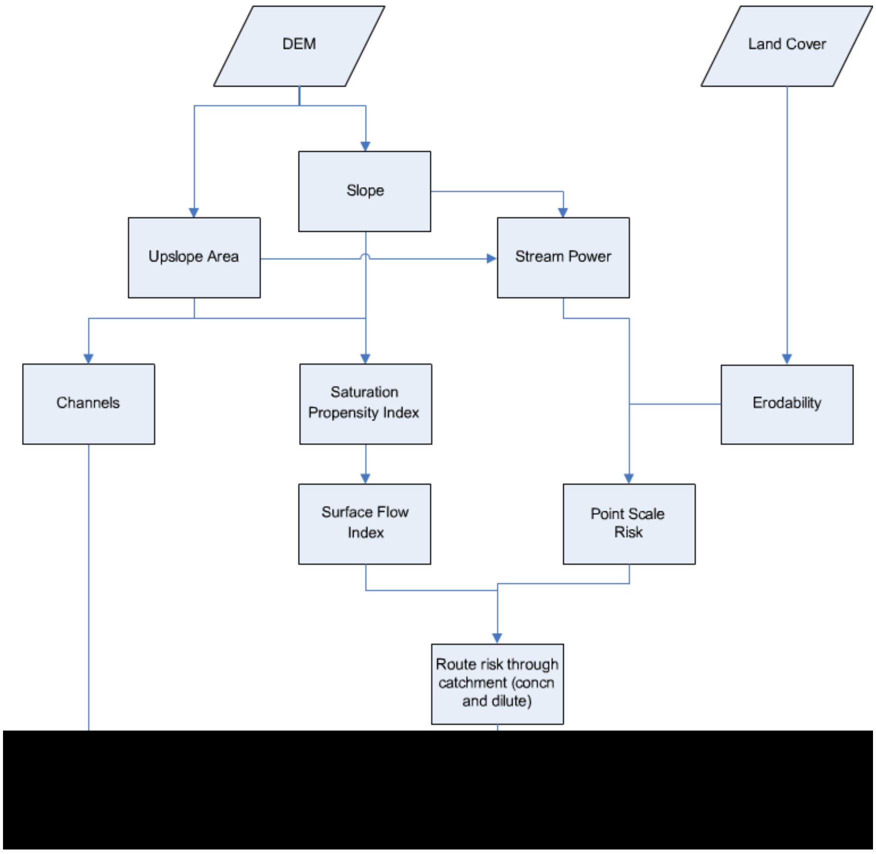


Figure 3.7: Conceptual flow chart model of the component of SCIMAP demonstrating how they interact (from: www.scimap.org.uk)

SCIMAP was run for 5,000 model simulations for the Esk in which land cover types were randomly assigned a risk weighting from 0 to 1 in each simulation. The resulting correlation coefficient was used to quantify the strength of relationship between in-stream concentrations and the risk estimates for each simulation. SCIMAP can be formulated to assume that nutrients are bound to sediment particles (e.g. phosphorus) and require fast flowing water to be entrained: in this case a stream power (sp) index is used to quantify the erosive potential in each cell. Alternatively SCIMAP can assume that the nutrients are entrained by solution (e.g. nitrate) in which case no stream power index is used. For the Esk SCIMAP was run both 'with stream power (*sp*)' and 'without stream power'.

Finally, SCIMAP was extended to the whole catchment as the land cover weightings that resulted in the highest correlations with the observed values for each land cover are applied. The resulting risk map is a derived from the land cover map (Centre of Ecology and Hydrology (CEH)) (Figure 3.3) and the hydrological connectivity (derived from the DTM). SCIMAP derives an in-stream risk value for every 10 m reach in the catchment which provides a reasonable resolution to construct an assessment of diffuse pollution risk.

3.7 Summary

This chapter has outlined the techniques that are utilised here to address the objectives that have been outlined in order to meet the aim of this work. Both practical fieldwork and laboratory methods are outlined alongside computational techniques that aid the practical elements. The resultant data is worked through in the following chapters in this work.

4.0 Spatial variations in water quality parameters in the River Esk

4.1 Introduction

Investigating the spatial distribution of water quality parameters is crucial to understanding how the landscape influences the properties of the river water. This chapter firstly reports the annual means for parameters analysed for within the monthly sampling system to show the spatial patterns across the catchment; linking to this is an analysis of the parameters relationship to each other. This is followed by a section 4.3 that investigates the influence of catchment size on these annual figures. This approach is then developed and in section 4.4 the influence of land cover considered upon the annual statistics.

4.2 Parameter Patterns

In the following section parameters analysed at a monthly timescale have been modified to create annual mean statistics; these are interrogated to explore the spatial patterns specific to parameters and between parameters. Anions and cations were analysed from October to May (8 months) and other parameters (pH, conductivity and dissolved oxygen were analysed using the YSI probe from February to May (4 months). These sampling periods do not represent a complete annual cycle, which was outside the scope of this study, and so may not reflect the annual means based on more complete data yet the derived annual statistics allow for relative (but not absolute) comparisons. The nitrate data recorded for May were calculated using the UV-vis detection method as opposed to the suppressed detection method due to co-elution of peaks on the Dionex analysis system. Spatial parameter analysis enables the tributaries to the Esk and the main stem to be compared. In Figures 4.1 to 4.4 tributaries can be identified by a black marker inside the coloured point. Many tributary sites were located close to the confluence with the Esk so as to capture the signals from each sub-catchment (see Chapter 3); in the following diagrams tributary points have been relocated to ensure an easier visual representation of the distinction between main stem sites and tributary sites. Data are presented for all parameters at levels that vary to a significant degree above the Dionex detection limits (see Chapter 3). Concentrations of ammonium, nitrite and phosphate had levels close to or below the detection limits found throughout the spatial monthly survey and therefore they are not investigated any further.

4.2.1 Spatial distribution of anions and cations

Figure 4.1 demonstrates how the annual concentrations of chloride and bromide vary over space within the Esk catchment study area. Firstly, it must be noted that it could be problematic to compare between diagrams due to varying scales/concentrations, yet this highlights the need to be aware of the scale. This approach is used to gain a thorough understanding of spatial trends of the individual water quality parameters.

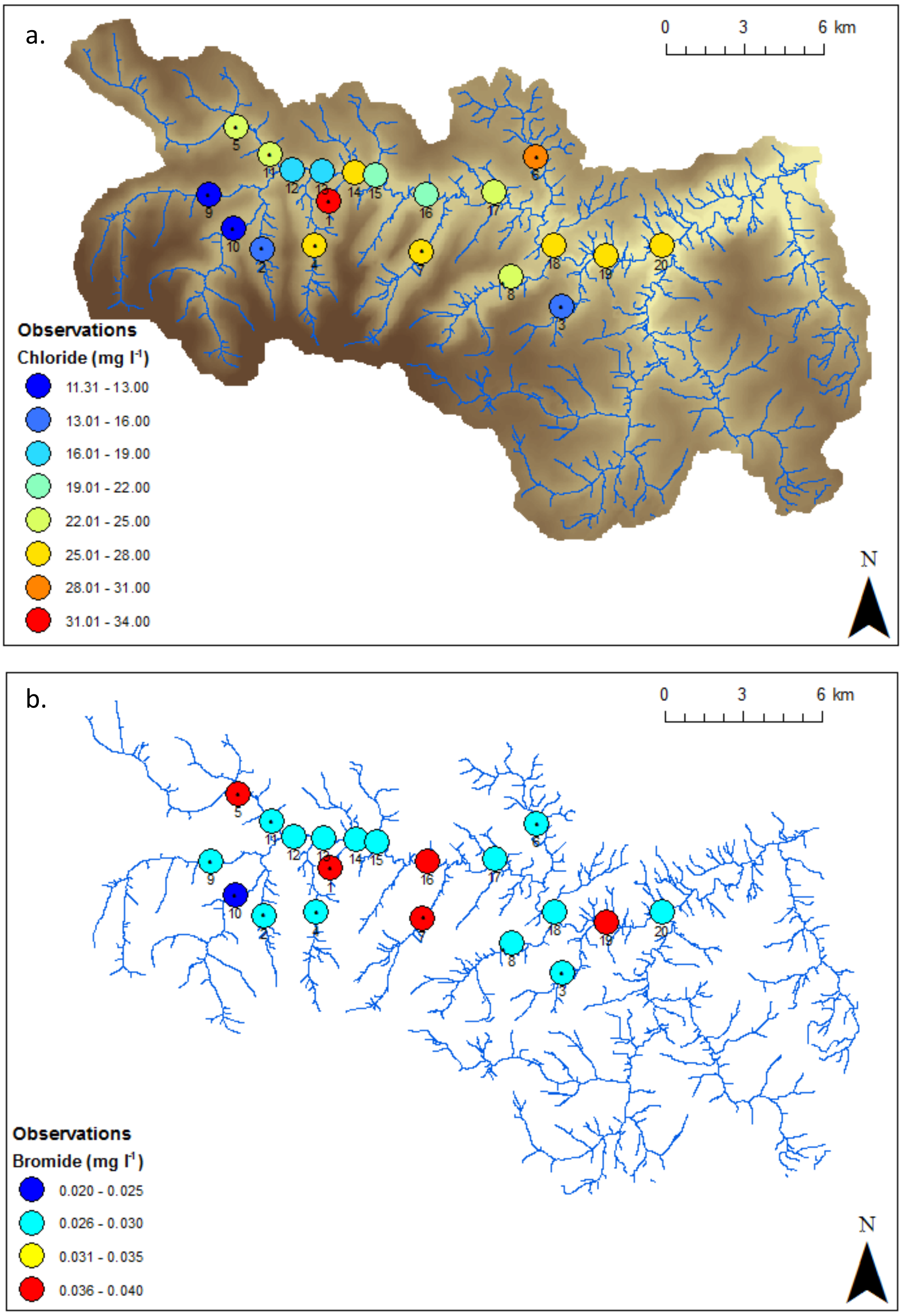


Figure 4.1: Spatial distribution of annual concentrations of selected anions; (a) chloride and (b) bromide

Chloride (Cl) annual concentrations (Figure 4.1a) display a trend similar to that of shown by sodium. There is evidence for a down-catchment increase in annual concentrations with higher values downstream in the main stem, i.e. the Esk at Grosmont, Esk at Egton Bridge and Esk at Glaisdale (21.1 mg l^{-1}, 20.3 mg l^{-1} and 20.9 mg l^{-1} respectively) and marginally lower concentrations upstream at sites such as Esk at Castleton and Esk at 6 Arches (17.7 mg l^{-1} and 17.3 mg l^{-1} respectively). This evidence of a down-catchment increase in concentration is substantiated by headwater tributaries annual concentrations; e.g. Hob Hole-12.1 mg l^{-1}, Westerdale Beck- 11.3 mg l^{-1} and Tower Beck- 15.3 mg l^{-1} are lower than lowland tributaries, e.g. Toad Beck- 31.5 mg l^{-1}, Stonegate Beck- 27.3 mg l^{-1}. These higher concentrations from certain tributaries seem to be diluted by the discharge in the main river. Chloride concentrations in pristine freshwater environments are usually lower than 10 mg l^{-1} (Chapman and Kimstach, 1996); one explanation that can be postulated is that the higher concentrations found in the Esk may originate from sea salt aerosols in precipitation and from the rivers proximity to the coast (Ward and Robinson, 2000). This may explain the higher concentrations at sites closer to the coast e.g. Esk at Grosmont (21.1 mg l^{-}1) against Esk at Castleton (17.7 mg l^{-1}). However a stronger east to west gradient in the chloride concentrations would be expected if this was the case, i.e. Butter Beck in the east has a similar concentration (13.80 mg l^{-1}) to headwater tributaries in the west. Other explanations could be chloride sources related to the varying geologies or land cover in the catchment and mobilised by chemical weathering or leaching respectively e.g. variability is injected into the system with higher annual concentrations found in Commondale Beck (e.g. Commondale Beck a- 19.3 mg l^{-1}). It appears that the geologies do not vary significantly over the catchment so chemical weathering is possibly not an explanation for varying concentration. Land cover will be explored as a mechanism of influence on parameter concentrations later in this chapter. Sodium annual concentrations demonstrate a similar trend with increasing concentrations downstream in the main stem and higher concentrations in lowland tributaries compared to headwater systems e.g. ~9.0- 11.0 mg l^{-1} in headwater tributaries to ~15.0- 16.0 mg l^{-1} downstream at Grosmont. The sodium in the Esk may result from similar sources to chloride e.g. sodium may vary in precipitation (Neal and Kirchner 2000).

Annual bromide (Br) concentrations (Figure 4.1b) can be likened to fluoride (F) concentrations. They both exhibit low values that do not fluctuate widely. At the majority of sample sites, Br concentrations consistently range between 0.026-0.030 mg l^{-1} (3 d.p.) with a number of higher levels that have been identified; Commondale Beck b, Toad Beck, Esk at Houlsyke, Great Fryup Beck and Esk at Egton Bridge (in red on Figure 4.1b). However increases are minimal. Most natural waters have a fluoride concentration of less than 0.1 mg l^{-1} which is the case in the Esk with values from 0.05-0.11 mg l^{-1} found. Annual F concentrations are slightly more variable than Br concentrations; similarly to the trends displayed by chloride and sodium a down-catchment increase in concentration emerges with the highest F concentrations recorded in tributaries

(Danby Beck, Toad Beck, Great Fryup Beck and Glaisdale Beck). Therefore this difference in concentrations may be related to increased dilution of the anion in the main stem alongside diffuse pollution and leaching influencing the water quality in these sub-catchments. As levels of these parameters are so low and close to the detection limits for the Dionex system, they will not form a major part of the rest of the study.

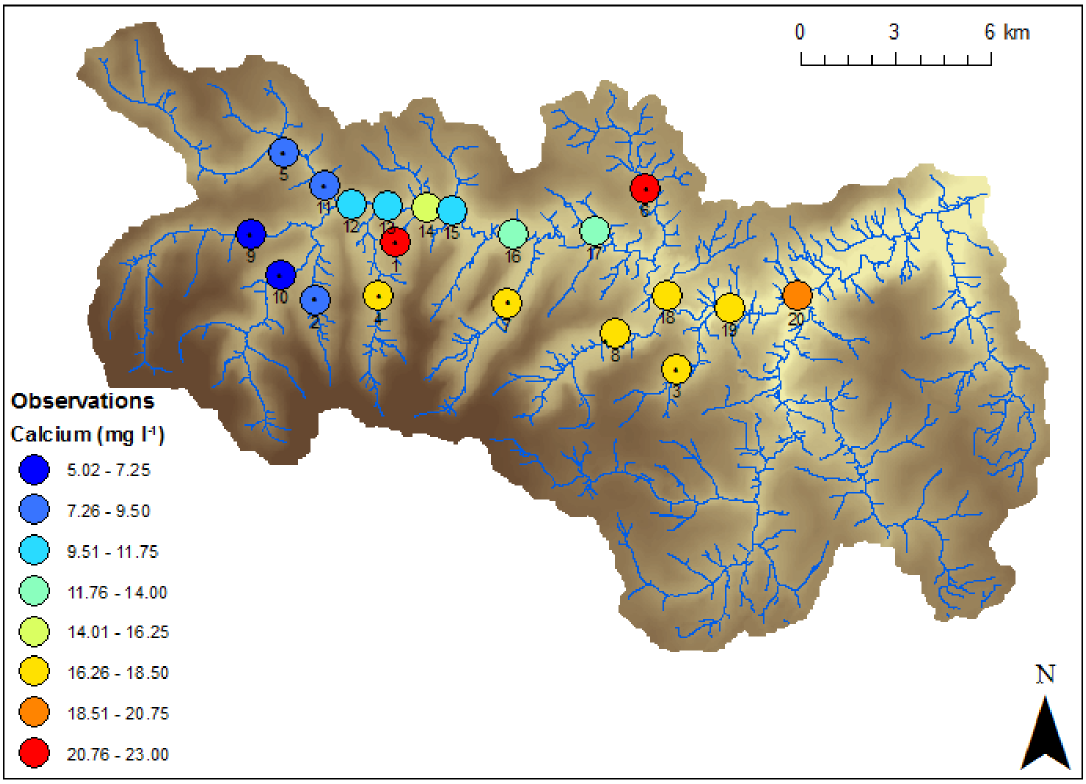


Figure 4.2: Spatial distribution of annual concentrations of calcium

Figure 4.2 illustrates the spatial differences in annual calcium concentrations; the trend presented is similar to that shown by sulphate and magnesium (see Appendix). Annual calcium (Ca) concentrations are lower in the headwater tributaries of the Esk; Commondale Beck a and b, Westerdale Beck, Hob Hole and Tower Beck have concentrations in the lowest range (5.0- 7.0 mg l^{-1}). Downstream of the headwater catchments, the sites on the Esk main stem also maintain low annual concentrations, yet variability is generated from the input of tributary sources; for example, Danby Beck and Toad Beck exhibit annual concentrations of 14.4 mg l^{-1} and 21.8 mg l^{-1} respectively. These higher concentrations are a result of the catchment properties and characteristics that influence the chemistry at the sample point. However, much of the variability is diluted out in the main stem and the majority of points on the main stem from upstream of Lealholm are ~10.0 mg l^{-1}, with the exception of the Esk at Danby Road Bridge which exceeds other upper-catchment main stem sites by ~2.0 mg l^{-1}. This could indicate the influence of the inputs from Toad Beck on the sample point at Danby Road Bridge which appears to demonstrate high annual concentrations of Ca. A gentle downstream gradient of increasing Ca concentration is present on the main stem with higher annual values at Glaisdale, Egton Bridge and Grosmont of ~14.0- 15.0 mg l^{-1} to contrast to those reported upstream. It can be inferred that this may be a consequence of the continued input of higher concentrations from tributaries because essentially water quality is a mixture of waters from tributaries of varying quality (Meybeck *et al.*, 1996); e.g. Stonegate Beck has the maximum annual Ca concentration of 22.9 mg l^{-1}. Secondly, it is fair to expect that this increase in concentrations is due to the influence of catchment characteristics and anthropogenic influences (Giller and Malmqvist, 1998). For example, Ca is a significant constituent of many common rock minerals (Hem, 1985) and therefore calcareous rocks resident in the Ravenscar Group geologies present in the catchment (see Chapter 3) may have greater influence on the water chemistry in certain areas.

As indicated above, annual concentrations of magnesium (Mg) and sulphate (SO_4) demonstrate a similar trend to Ca within the Esk catchment. A downstream gradient prevails on the main stem with lower concentrations in the upper catchment sites such as the Esk at 6 Arches, the Esk at Castleton and the Esk at Danby Moors Centre (Mg: ~3.0 mg l^{-1}; SO_4: ~4-5 mg l^{-1}) compared to higher concentrations in at lower catchment sites e.g. Esk at Glaisdale, Egton Bridge and Grosmont (Mg: ~4.0 mg l^{-1}; S: ~6.0 mg l^{-1}). The Ca pattern is also paralleled by the lower concentrations in headwater tributaries e.g. Hob Hole (Mg: 2.7 mg l^{-1}; S: 3.9 mg l^{-1}) and higher concentrations in the lowland tributaries e.g. Great Fryup and Stonegate Beck (Mg: 5.9 mg l^{-1}; S: 7.1 mg l^{-1}). Magnesium contributes, with calcium, to water hardness (Chapman and Kimstach, 1996) and thus a similar down-catchment increase in concentration can be expected. This downstream gradient is not unusual and should be considered prevalent in river systems (Giller and Malmqvist, 1998).

Potassium and nitrate are key nutrients, often considered to be macro-nutrients. Nitrate is thought to be of particular importance to the freshwater pearl mussels habitat. As discussed in relation to the above parameters, aspects such as climate and chemical weathering do affect chemical composition of freshwaters; however, land use (and thus land cover) probably has the major impact on nutrients in the river system (Giller and Malmqvist, 1998). Thus they require particular focus when considering the spatial distribution of water quality parameters in the Esk.

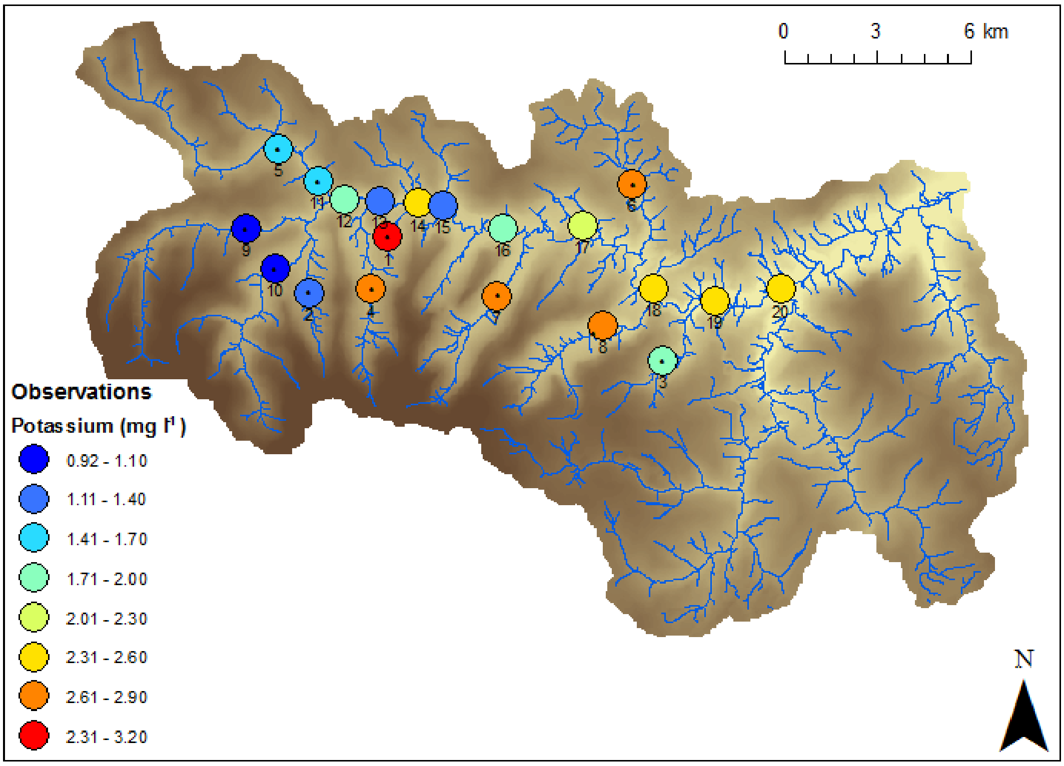


Figure 4.3: Spatial distribution of annual concentrations of potassium

Potassium, like other anions/cations discussed above, demonstrates an increase down catchment in concentration; values rise from ~1.0 mg l^{-1} in the headwaters to ~2.0 mg l^{-1} at the lower study catchment sites (see Figure 4.3). Variation is introduced via tributaries Toad Beck, Stonegate Beck and Great Fryup Beck. This may be explained by land use practices in these areas and leaching from lowland fields into the river system. It is also apparent that this signal is dampened via dilution from the main stem as concentrations are not maintained at these levels. This downstream increase in parameters can be attributed to 'change in geology, soils, climate, vegetation, and in anthropogenic influence as one moves from uplands to lowlands' (Giller and Malmqvist, 1998: 53). The land cover influence will be investigated further in section 4.4. However, as potassium is less mobile than important anions phosphate and nitrate potassium leaching losses from fertilised land is not expected to be as significant (Stott and Burt, 1997). Therefore to consider nitrate is an important aim.

Nitrate is a key parameter in this investigation (e.g. Skinner *et al.*, 2000) so deserves more detailed discussion. Figure 4.4 presents the annual concentrations from the twenty sites analysed over the study period. This diagram allows the spatial variation, or lack of variation, to become apparent. Over 75% of sites displaying an annual mean less than 1.1 mg l^{-1}. There is a tendency towards lower concentrations in the upper catchment sampling points such as Hob Hole and Westerdale Beck, compared to lower catchment sites such as Egton Bridge and Grosmont; concentrations are found to be almost double in many cases. The increase in annual nitrate concentration with distance downstream can be explained by a subtle increasing signal of leachate reaching the watercourse which is obviously exacerbated further downstream as the river is exposed to a larger area. This concept is tied to the composition of the land cover evolving in different ways and in different areas in the Esk's catchment. This will be examined later in greater depth; initially it can be hypothesised that the annual nitrate concentrations are lower in the upper catchment as there is a lower percentage of pastoral and arable farming and a higher proportion of moorland, whereas in the lower catchment, where the topography is more conducive to farming, there are higher annual concentrations of nitrate due to leaching of material applied to fields. This trend was discovered by de Becker *et al.* (1984, referenced by Giller and Malmqvist, 1998) who found nitrate concentration to decrease as the areas of agricultural land decreased. This land cover influence upon nitrate is be explored in section 4.4.

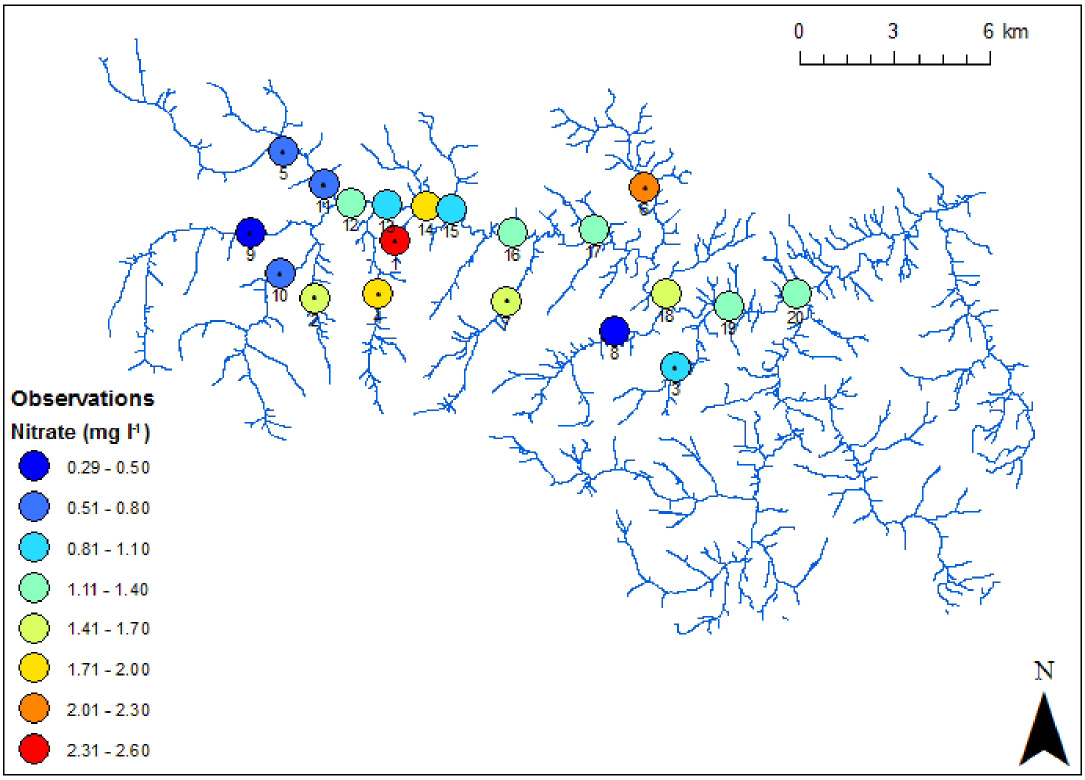


Figure 4.4: Spatial distribution of annual concentrations of nitrate

Heterogeneity within natural systems is common, even at the level of nitrogen cycling, both spatially and temporally (McClain *et al.*, 2003). This natural variance modifies aspects of the water from site to site via 'sources, pathways and interactions with particulates' (Meybeck *et al.*, 1996: 253). McClain *et al.* (2003: 301) postulate the phrase of biogeochemical hot spots that relates to 'patches [of land] that show disproportionately high reaction rates relative to the surrounding matrix'. This differs slightly to the definition of hot moments that McClain *et al.* (2003:301) provide, 'short periods of time that exhibit disproportionately high reaction rates relative to longer intervening time periods'. When assessing Figure 4.4, is it possible to begin to hypothesise about the presence of hot spot sites of higher biogeochemical activity. Danby Beck, Toad Beck, the Esk at Danby Road Bridge and Stonegate Beck which generate annual concentrations of 1.2 mg l^{-1}, 2.6 mg l^{-1}, 1.2 mg l^{-1} and 1.6 mg l^{-1} respectively can be identified as hot spot sites. The concentrations at Danby Road Bridge may be influenced by the mixing of the input of the Toad Beck (the maximum nitrate concentration found in the system). It must be noted that these are only sample points *in-river* with high nitrate values, in other words we can only identify the sub-catchment of the components derivation and not the specific land component within the sub-catchment. On the other hand, both land use (and thus land cover) and topography influence nitrate losses from a catchment (Armstrong and Burt, 1993) and so these factors must be considered alongside naturally varying biogeochemical areas for the reason for higher concentrations. McClain and colleagues indicate that disturbances (such as anthropogenic influences) can increase the rates of reaction at sites (McClain *et al*., 2003). It is likely that land use practices in these particular catchment sub-systems heighten the source components that contribute nitrate to the catchment. Nevertheless, identification of 'concentration hot spots' will focus future management mechanisms and practices on areas of land that should be acted upon.

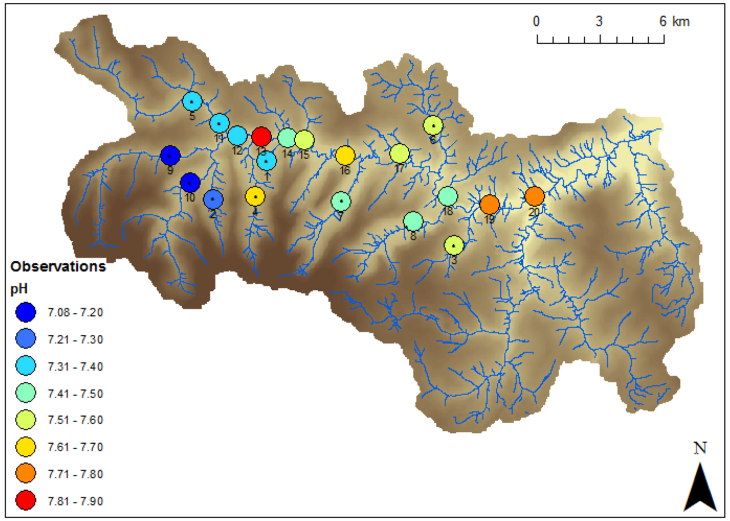
4.2.2 Spatial distribution of other parameters

Figure 4.5 summarises the annual values of water quality parameters conductivity, dissolved oxygen and pH allowing a deeper understanding in the spatial attributes of the catchment. All the sites annual pH records vary from a minimum of 7.08 pH at Westerdale Beck to a maximum of 7.90 pH at the Esk at 6 Arches (see Figure 4.5a). The majority of the upper catchment tributaries, despite some variation, are approximately neutral (~7.00pH) compared to sites further down the catchment which are slightly alkaline. The pH at sites on the main stem increase and range from 7.44 pH to 7.90 pH.

Annual figures of both conductivity and dissolved oxygen increase at sites in the main stem compared to the headwater sub-catchments (Commondale Beck, Westerdale Beck, Hob Hole and Tower Beck). Annual conductivity figures are lowest in the western (upper-catchment) tributaries e.g. Hob Hole- 52 μS cm^{-1} and Figure 4.5b demonstrates that conductivity rises will distance down catchment to values over 100 μS cm^{-1} downstream of Lealholm in the Esk. However, there are sites that have relatively high values (relative to other sites on the Esk) in the study area at Danby Beck, Toad Beck and Stonegate Beck (120 μS cm^{-1}, 160 μS cm^{-1}, 149 μS cm^{-1} respectively); conductivity is dictated by the geological nature of the catchment (Webb and Walling, 1992) and therefore the separate components to these sub-catchments will induce a different signal on water quality, creating variable conductivity values across a catchment. Whilst certain tributaries exhibit higher values than others it is important to note that these are still low solute poor values in relation to many UK rivers.

Dissolved oxygen echoes this pattern with increasing percentages with distance down catchment; evidence of this pattern is strengthened by the fact that the highest annual dissolved oxygen levels are found in the Esk at Glaisdale and the Esk at Egton Bridge (134.0% and 137.0% respectively) whereas the lowest levels are found in the upper catchment at the Esk at 6 Arches and Danby Beck (116.3% and 113.5% respectively) (see Figure 4.5c). This down catchment increase in dissolved oxygen may relate to an increase in channel velocity down catchment which increases oxygen exchange between air and water (Walling and Webb, 1992).

a.



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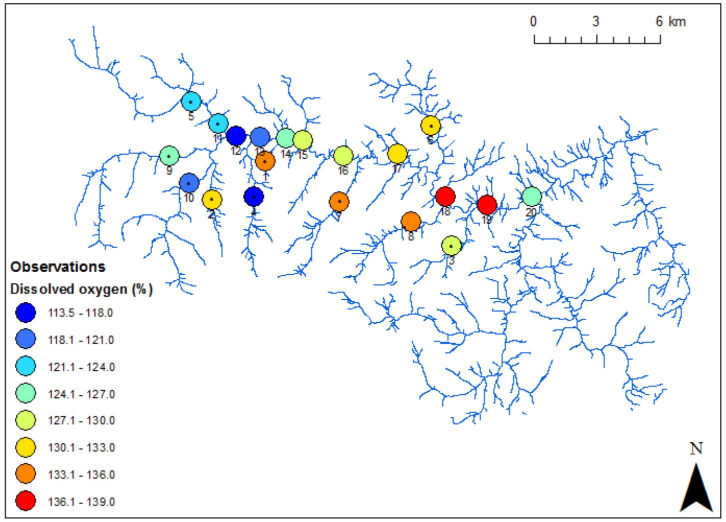

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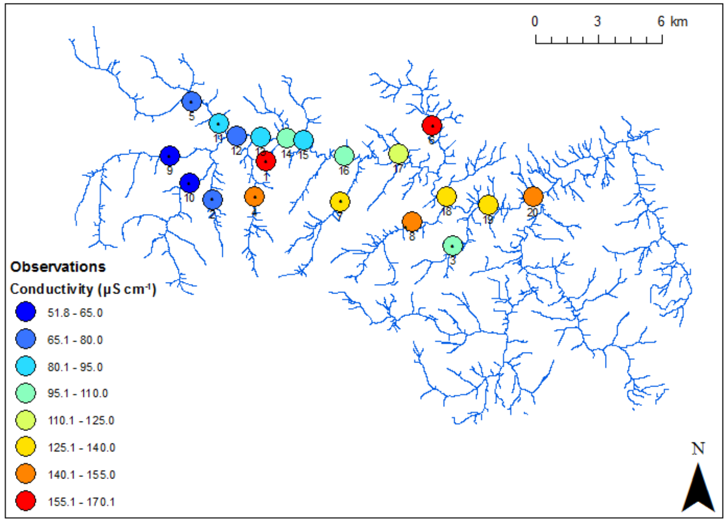


Figure 4.5: Diagrams to represent the spatial distribution of annual figures for parameters (a) pH, (b) conductivity and (c) dissolved oxygen

4.2.3 Inter-variable relationships

To further understand the spatial patterns among the variables investigated, linear correlation was performed on all combinations of the data to get an impression of which parameters are associated and demonstrate the same trend. For example, does an increase in chloride at Grosmont also mean an increase in sodium? Linear correlation investigates the relationship that exists between two variables. However, it is important to state that ‘correlation is not causation’. Therefore a high correlation does not indicate that a parallel increase in another variable has resulted from this alteration in the system i.e. it cannot be described as a causal relationship. The relationships discussed analysed below were generally found to be linear in preliminary analysis. The Pearson’s correlation coefficients r-values between the parameters spatially represented in sections 4.2.1 and 4.2.2 are displayed below in Table 4.1.

Table 4.1: Pearson's correlation coefficient r-values for the relationships between variables; at 18 degrees of freedom (as n=20) 95% significance level= +/-0.44 (*); 99% significance level= +/-0.56(**); 99.9% significance level= +/-0.68 (***)

VARIABLE	F	Cl	NO_2^-	Br	S	NO_3^-	PO_4^{-3}	Na	NH_4	K	Mg	Ca	Conductivity	pH	DO
Fluoride (F)		0.40	0.07	0.30	0.87***	0.30	-0.03	0.55*	0.42	0.65**	0.53*	0.47*	0.58**	0.25	0.35
Chloride (Cl)	-		0.14	0.46*	0.64**	0.83***	-0.07	0.97***	0.52*	0.91***	0.89***	0.86***	0.90***	0.36	0.24
Nitrite (NO_2^-)	-	-		-0.37	0.01	0.16	-0.16	0.12	0.06	0.07	0.06	0.11	0.12	0.35	-0.43
Bromide (Br)	-	-	-		0.34	0.35	-0.09	0.48*	0.41	0.46*	0.38	0.28	0.36	0.30	0.42
Sulphate (SO_4)	-	-	-	-		0.52*	-0.16	0.70***	0.59**	0.84***	0.80***	0.78***	0.82***	0.30	0.48*
Nitrate (N)	-	-	-	-	-		-0.09	0.78***	0.49*	0.82***	0.81***	0.78***	0.75***	0.10	0.24
Phosphate (PO_4^{-3})	-	-	-	-	-	-		-0.06	-0.10	-0.18	-0.15	-0.13	-0.10	0.09	0.06
Sodium (Na)	-	-	-	-	-	-	-		0.47*	0.93***	0.87***	0.81***	0.89***	0.35	0.27
Ammonium (NH_4)	-	-	-	-	-	-	-	-		0.56**	0.48*	0.45*	0.46*	0.15	0.07
Potassium (K)	-	-	-	-	-	-	-	-	-		0.95***	0.91***	0.94***	0.29	0.40
Magnesium (Mg)	-	-	-	-	-	-	-	-	-	-		0.98***	0.96***	0.30	0.43
Calcium (Ca)	-	-	-	-	-	-	-	-	-	-	-		0.96***	0.37	0.42
Conductivity	-	-	-	-	-	-	-	-	-	-	-	-		0.40	0.44*
pH	-	-	-	-	-	-	-	-	-	-	-	-	-		0.06
Dissolved oxygen (DO)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	

Many of the correlation coefficients are insignificant and close to 0 e.g. pH correlated against all variables, in these cases we cannot state with a significant level of confidence that there is a relationship between the two variables. Nevertheless the correlation coefficients for many of the variables exhibit values allow the conclusion that with 99.9% confidence we can state that a relationship exists. Typically correlation coefficients are positive which demonstrates positive correlation between parameters as opposed to negative correlation (e.g. values close to -1). For example in Figure 4.6, magnesium and sulphate display a relationship (positive) that suggests that higher concentrations of one would indicate higher concentrations of the other.

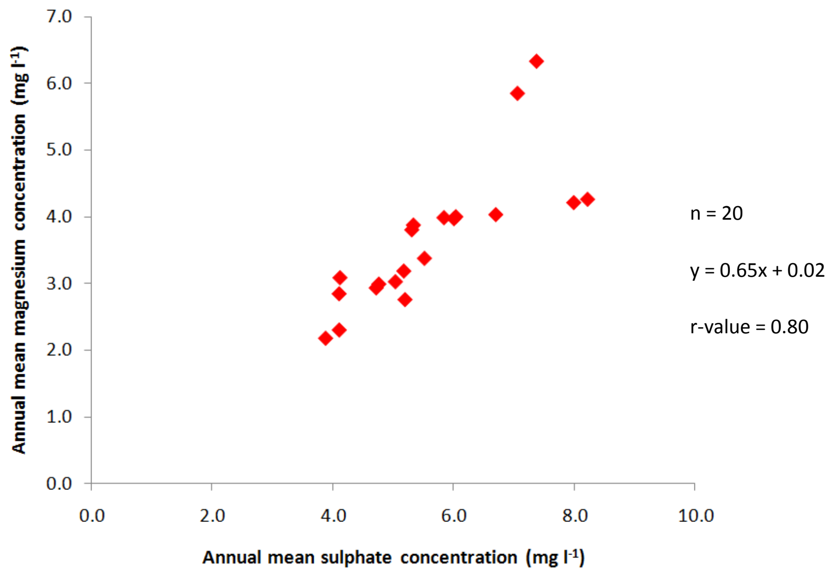
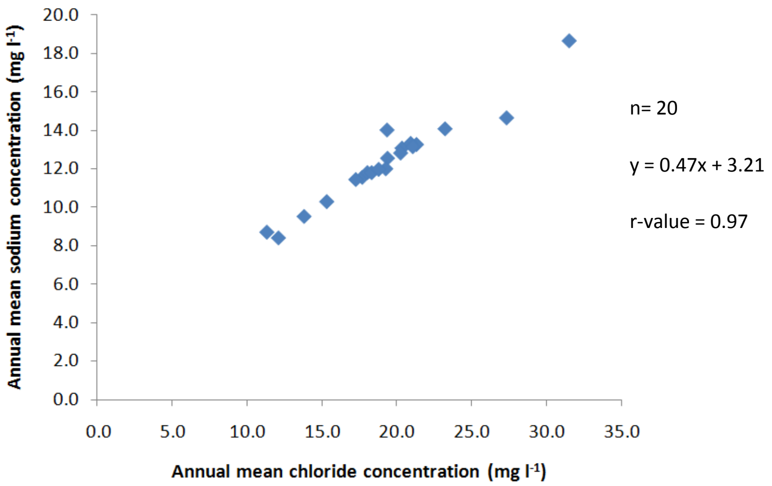


Figure 4.6: Relationship between annual mean concentrations of sulphate and magnesium from all sites investigated in the Esk catchment

However, there is noise present within this record and relationships that could be described as 'more linear' have been found. Overall in Table 4.1, twenty-seven of the relationships could be referred to with 99.9% confidence level in the relationship (see ***). A number of these relationships are displayed graphically in Figure 4.7.



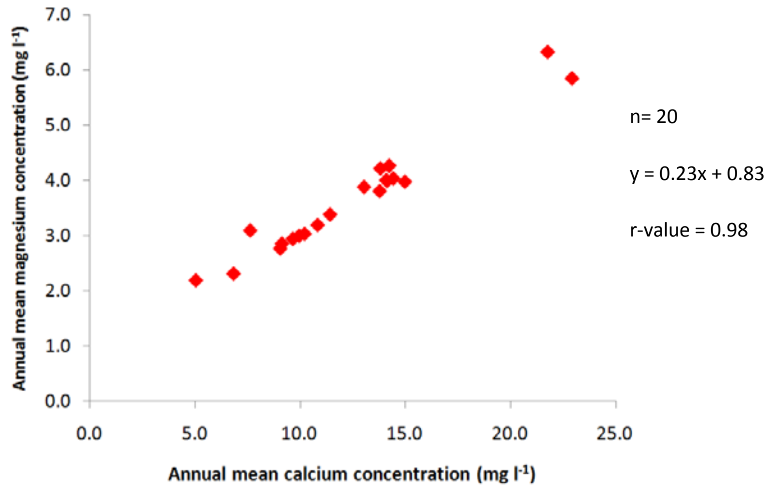


Figure 4.7: Examples of relationships between variables with high r-values

The relationships presented in Figure 4.7 have the some of the highest correlation coefficients found in the dataset, which allows for a confidence level of 99.9% that a relationship exists. Firstly, the high correlation coefficient between sodium and chloride would be expected as they commonly exist is the strong ionic compound of sodium chloride (NaCl). Both Na^+ and Cl^- are considered to be atmospheric inputs and present in rainfall; amounts of these solutes can vary relating to their proximity to the coast and precipitation intensity (Meybeck *et al.*, 1996; Ward and Robinson, 2000; Webb and Walling, 1992). This result coroborates with Neal and Kirchner (2000) who also found strong linear relationships between sodium and chloride concentrations in streams in the Afon Hore, Wales. Secondly, in the case of magnesium and calcium, both ions can be attained from chemical weathering of minerals by carbonic acid (Meybeck *et al.*, 1996). Thus, if chemical weathering is occuring within the catchment, the variable release of ions from groundwater into the Esk and its tributaries may explain the relationship. Also, water hardness is a measure of the concentraiton of calcium and magnesium ions (Ca^{2+} and Mg^{2+}) (Giller and Malmqvist, 1998); therefore to find a strong relationship between the two components in the system is unsurprising.

A number of high correlation coefficients that relate a specific variable to conductivity (magnesium, calcium, potassium and chloride) are present in Table 4.1. As conductivity is sensitive to variations in dissolved solids, particularly mineral salts (Chapman and Kimstach, 1996), it fair it hypothesise that these four variables make key contributions to the conductivity trend within the system i.e. when these variables are more concentrated this causes a parallel rise in the conductivity. The correlation coefficients allow the assertion that there is 99.9% confidence that there is a relationship between each of these minerals and conductivity. However, as indicated earlier, 'correlation does not mean causation' therefore this is only evidence to postulate this point and not proof of this point.

4.3: Spatial results: Catchment size trends

To analyse the influence of catchment area upon monitored parameters areas were derived using the method described in Chapter 3. The resulting areas could be referred to as the contributing areas to that particular sample point (the upslope land). The areas derived are presented in Table 3.1 (see Chapter 3).

Table 4.2: Catchment areas for all sample points in the Esk catchment

SITE	TRIBUTARY *or* ESK MAIN STEAM	CATCHMENT AREA (km^2)
Toad Beck	Tributary	1.8
Tower Beck	Tributary	6.7
Butter Beck	Tributary	8.8
Danby Beck	Tributary	12.4
Commondale Beck b	Tributary	13.7
Stonegate Beck	Tributary	13.9
Great Fryup Beck	Tributary	14.2
Glaisdale Beck	Tributary	15.4
Hob Hole	Tributary	17.5
Westerdale beck	Tributary	19.2
Commondale Beck a	Tributary	24.6
Esk at Castleton	Esk	74.6
Esk at 6 Arch Bridge	Esk	88.4
Esk at Danby Road Bridge	Esk	95.9
Esk at Danby Moors Centre	Esk	96.6
Esk at Houlsyke	Esk	110.8
Esk at Lealholm	Esk	129.3
Esk at Glaisdale	Esk	160.3
Esk at Egton Bridge	Esk	188.2
Esk at Grosmont	Esk	284.7

There is a good range of catchment areas. All the upstream contributing areas of sample sites on tributaries are equal to or less than 25 km^2 whereas the contributing areas on the main stem vary from under 100 km^2 to ~290 km^2. The tributaries are distributed throughout the study catchment area, in both the headwaters e.g. Commondale Beck sites, Hob Hole and the lowland valley areas e.g. Butter Beck, Great Fryup Beck (see Chapter 3). It is logical that sample points within the main Esk increase by a greater magnitude downstream as they are exposed to a greater spatial extent as the river progresses.

Figure 4.8 represents the annual average nitrate concentrations recorded at the 20 spatial monitoring sites against the catchment area of the river at that specific point. Annual nitrate concentrations vary from 2.6 mg l^{-1} (in Toad Beck) to 0.3 mg l^{-1} (in Hob Hole). Toad Beck and Hob Hole have contributing areas of 1.8 km^2 and 17.5 km^2 respectively. The catchment areas extend to 284.7 km^2 at Grosmont, the maximum downstream spatial sampling point in my study.

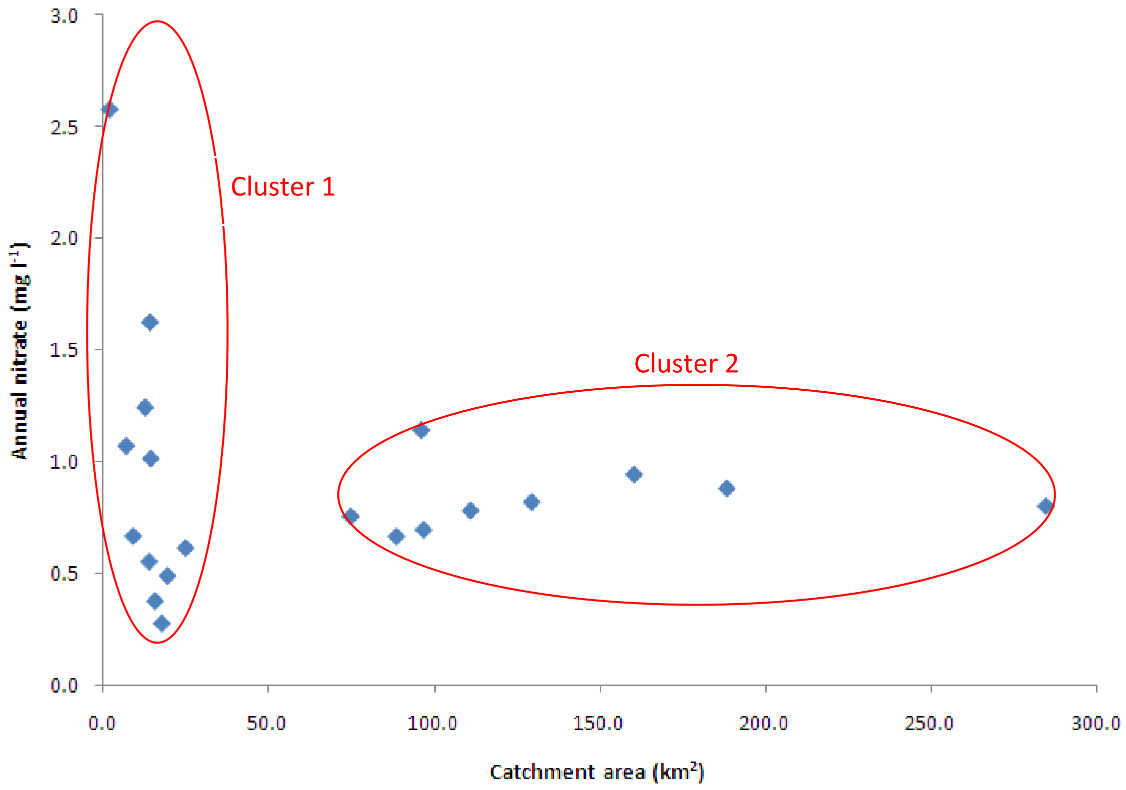


Figure 4.8: The relationship between annual average nitrate concentrations and catchment areas

Two clusters become distinct through analysing the data, indicated by cluster 1 and cluster 2 in Figure 4.8. The presence of these clusters exhibits a pattern of greater variability among nitrate concentrations within catchments with smaller catchment areas (cluster 1) opposed to reduced variability in nitrate concentrations at sites with larger catchment areas (cluster 2). Cluster 1 with greater variability contains all the tributaries that are sampled in the spatial strategy. Cluster 2 with lower variability is found at sites that have catchment areas all greater than ~75 km^2. When investigating further it is revealed that in cluster 1 all points are from tributaries and in cluster 2 all points are from sites on the main stem of the Esk. As previously acknowledged, the majority of tributaries are located in the upper headwaters, yet sites do include lowland tributaries e.g. Butter Beck (see Chapter 3).

Cluster 1 has a relatively large range of nitrate concentrations from a maximum of 2.6 mg l^{-1} in Toad Beck to a minimum of 0.3 mg l^{-1} in Hob Hole. This suggests that in smaller catchments the catchment characteristics e.g. topography, geology, soils as well as land cover and land management practices have a greater (more direct) influence on the monitored levels. This does not necessarily always result in high nitrate levels. Essentially in smaller catchments these factors are a larger driver of in-stream solute concentrations. Independent to catchment size, it can be noted that headwater tributaries have lower annual nitrate concentrations compared to lowland tributaries; this is likely to be related to catchment features such as land cover and this will be scrutinised in greater depth in section 4.4.

It is likely that the lack of variability within cluster 2 is due to the nitrate concentration diluted by the extra discharge present at the sample points which dilute the signal that may be generated from the surrounding land. For example, the Murk Esk may dilute the nitrate concentration at the Grosmont site. It is logical that the areas of sites within cluster 2 increase in this gradual manner as a downstream site includes the area of any upstream site. All concentrations in the main stem remain just below the 1 mg l^{-1} limit postulated by Skinner *et al.* (2003) varying from 0.7 mg l^{-1} to 0.9 mg l^{-1}; with the exception of the Esk at Danby Road Bridge which has an annual mean of 1.1 mg l^{-1}. It is likely that the elevated main stem nitrate concentrations at Danby Road Bridge could denote the influence of the high nitrate concentrations inputted from Toad Beck. It may also suggest that the adjacent catchment characteristics (e.g. soils, drainage) and land cover may impact the nitrate concentration in the main stem as can be seen in Toad Beck.

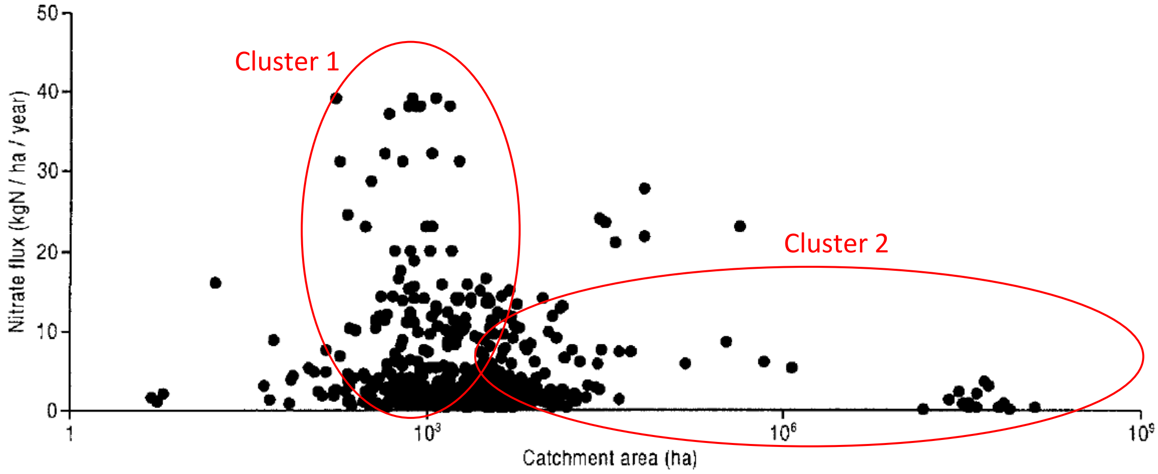


Figure 4.9: 'Relationship between drainage basin area and nitrogen fluxes in Europe and North America' (modified from Burt and Pinay, 2005: 298)

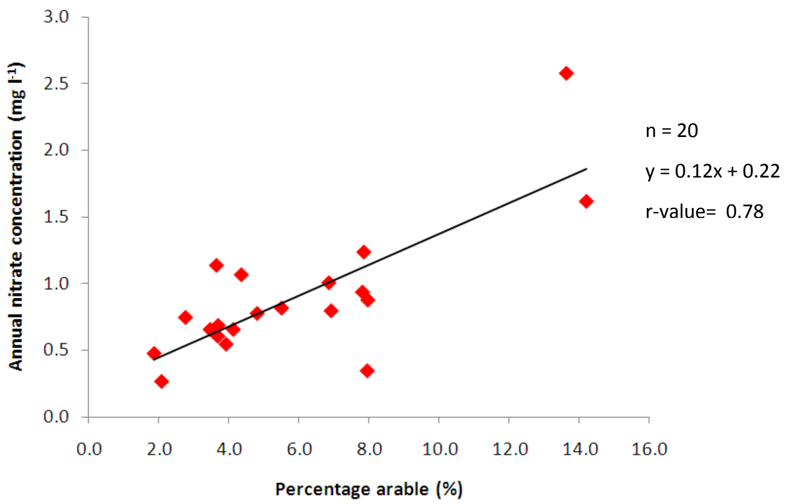
This overall trend exhibited in Figure 4.8 of greater variability in nitrate concentrations in catchments with smaller areas and lower variability in nitrate concentrations in larger catchments has previously been demonstrated by Burt and Pinay (2005) (Figure 4.9). However, this does differ in that data are from multiple basins spread over Europe and North America and also at a larger scale considering basins up to ~10^9 ha compared to data discussed here from multiple sites within one catchment with the maximum area <300 km^2. Nevertheless two clusters become visible within the cumulated data even considering the differences between catchments that will be present in the dataset. The clusters have been identified on Figure 4.9 as cluster 1 and 2. In cluster 1 nitrogen fluxes are more variable (values ranging from <10 kg N/ha/year - ~40 kg N/ha/year) whereas in cluster 2 this variability is reduced (values all <10 kg N/ha/year). Burt and Pinay (2005:298) suggest this pattern shows that 'subtle changes in land-management practices cannot be detected at the basin outlet' which agrees with the application of Figure 4.8. This may be due to the fact that at the basin outlet solutes that may have contributed to a stronger signal upstream will be diluted downstream due to higher discharges. Thus, the influence of solute concentration drivers (e.g. land cover) are captured within smaller scale catchments yet as the catchment size increases the driver signal is dampened/lost.

Finally, by reporting annual averages within the catchments, it is probable that monthly variability (both within the month and between months) is removed. However, catchment area can be considered to be a influencing factor over the nitrate concentration yet catchment dynamics and characteristics such as quickflow dominated or baseflow dominated, nutrient rich or nutrient poor, geology type and land cover (see section 4.4) must be investigated alongside drainage basin area.

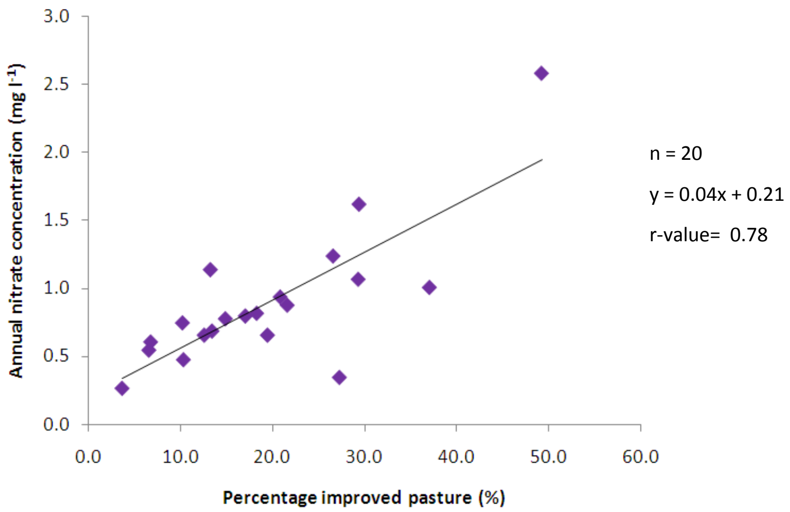
4.4: Land cover patterns

Land use influences water quality as it changes both spatially and temporally (Baker, 2003); also in a catchment like the Esk, dominated by surface and near-surface runoff, a close link between land use (and thus land cover) and water quality can be expected (giving a limited delay in land cover driver-response). The rural environment has become more varied in its make-up as diversification and intensification have occurred and now it is a different composition to that of the past (Burt and Johnes, 1997). Percentages of land cover that are exposed to the channel upper stream/catchment of the sample point were derived (see Chapter 3). To begin to gain an understanding of whether the catchment land cover composition affects the water quality components particular anions and cations have been compared to monitor trends between these factors. As nitrate is a significant nutrient both to pollution levels in river systems (Heathwaite *et al.,* 1993) and to the pearl mussel (Skinner *et al.,* 2003) and secondly as 'the effects of land use and land use change on stream nitrate and poorly understood' (Poor and McDonnell, 2007:332) it is the parameter focussed on here. Figure 4.10 demonstrates the influence of arable land, improved grassland and moorland on annual nitrate concentration from all 20 sites (tributary sub-catchments and main stem sites).

(a)



(b)



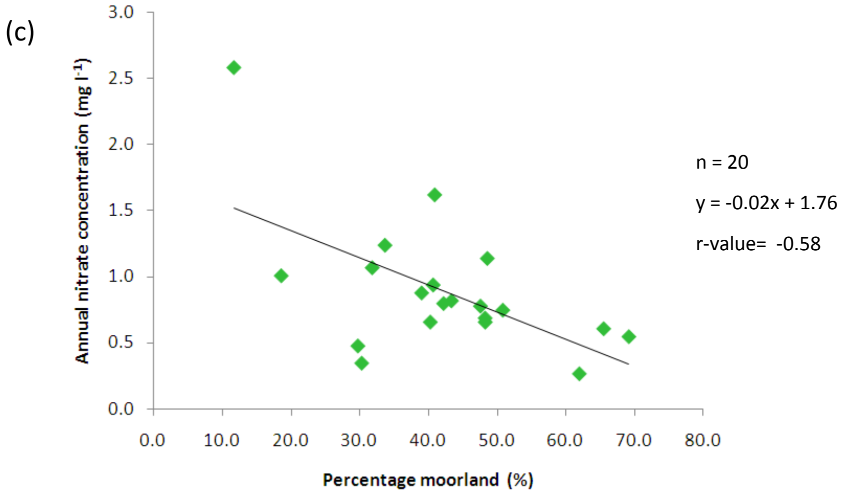


Figure 4.10: Relationship between annual nitrate concentrations and the three most dominant land cover catergories within the study area in the Esk catchment, (a) arable, (b) improved pasture, and (c) moorland (at 18 degrees of freedom (as n=20) 95% significance level= +/-0.44; 99% significance level= +/-0.56; 99.9% significance level= +/-0.68)

Arable land and improved pasture display a similar trend of positive correlation and an increase in nitrate concentration with an increase in percentage of the land cover catergory. Therefore as the area of land utilised for the crop production/holding livestock increases, there is typically an increase in the amount of nitrate exported to the river. This nitrate is typically sourced from livestock and animal waste and inorganic fertilisers (Heathwaite *et al.,* 1996). The applied fertilisers can be mobilised and transported primarily by sub-surface water movement to the the watercourse, leaching, as well as in overland flow or from soil erosion. Livestock grazing on the slopes or in the lowlands can compact land increasing runoff which reduces infiltration rates into the fields and add to the available nitrate by their outputted waste (Heathwaite, 1993). This evidence of high nitrate concentrations in sub-catchments with higher percentages of arable and improved pasture is corroborated by Buck *et al.* (2004) who found nitrate to correlate well with area of pasture in sub-catchments within an area. The Pearson's correlation coefficient r-value in Figure 4.10a (0.78), significant at the 99.9% confidence level, agrees with research assembled by the Royal Society (1983; referred to by Burt and Arkell, 1987) that indicated nitrate in watercourses to typically be mobilised via leaching from arable land. Secondly, the correlation coefficient in Figure 4.10b (0.78), again significant at the 99.9% confidence level, supports Ryden *et al.* (1984) who demonstrated that another significant source of leached nitrate is from intensively managed grasslands.

Toad Beck has an annual nitrate concentration of 2.6 mg l^{-1} which is almost 1.0 mg l^{-1} greater than all other annual concentrations and therefore is the most notable outlier from the best fit lines in Figure 4.10. Previously, it would of been posssible to dismiss the high concentrations in this tributary due to its smaller size and therefore the lack of dilution from water from elsewhere in the system. However, the percentages of arable land and improved pasture in Toad Beck are 13.6% and 49.2% respectively; this the highest percentage derived at all the 20 sites of improved and one of the highest of arable land. Therefore, this evidence adds to the contention that this sub-catchment is a problematic sub-basin and a source of pollution in the system due to the land cover itself. On the other hand, it appears that the higher the percentage of moorland land cover in the upstream catchment, the lower the annual nitrate concentration, as illustrated by Figure 4.10c. Nitrate concentration is negatively correlated with percentage moorland with a correlation coefficient of -0.58 and is significant at the 99% confidence interval. In moorland areas fertiliser application will not be undertaken and and vegetation will buffer the movement of nitrate to the watercourses.

Table 4.3 displays the Pearson's correlation coefficient r-values for the relationships between the three main land cover types and selected other parameters; calcium, chloride, potassium, magnesium, sodium and sulphate (selected on the basis of their spatial variability). The correlation coefficients for arable and improved pasture, which are mostly significant at the 99.9% confidence level, suggest there the catchment land cover does influence the concentrations found in the adajacent river water. Likewise the relationship between moorland and the variables illustrate a pattern of weak negative correlation. However the trends between improved pasture and arable land for these parameters also reflects that found with nitrate as discussed above.

Table 4.3: Pearson's correlation coefficient r-values for the relationship between land cover types and selected variables; at 18 degrees of freedom (as n=20) 95% significance level= +/-0.44 (*); 99% significance level= +/-0.56(**); 99.9% significance level= +/-0.68 (***)

VARIABLE	ARABLE		IMPROVED PASTURE		MOORLAND	
	r-value	Correlation trend	r-value	Correlation trend	r-value	Correlation trend
Calcium	0.93^{***}	Positive	0.78^{***}	Positive	-0.57^{**}	Negative
Chloride	0.87^{***}	Positive	0.67^{**}	Positive	-0.37	Negative
Potassium	0.89^{***}	Positive	0.84^{***}	Positive	-0.63^{**}	Negative
Magnesium	0.94^{***}	Positive	0.82^{***}	Positive	-0.59^{**}	Negative
Sodium	0.83^{***}	Positive	0.70^{***}	Positive	-0.44^{*}	Negative
Sulphate	0.77^{***}	Positive	0.86^{***}	Positive	-0.75^{***}	Negative

Nevertheless, in light of the trends exhibited, as discussed above correlation is not necessarily an indication of causation and thus other possible factors involved must be acknowledged; natural factors such as topography and soil type (Baker, 2003) influence the water quality and will affect concentrations in the catchment. For example, Burt and Arkell (1987) postulate that nitrate export via leaching can be assisted by these natural factors, which are spatially variable, to modify water movement. Secondly, it should be noted that many sites analysed are not independent and are influenced by sites upstream. However the evidence presented strongly suggests that land cover is the dominant control on water quality and the trends are compelling in light of the fact that 'understanding of the cumulative contributions of different land uses as they change downstream may be a vital ingredient for successful water management' (Buck *et al.*, 2003:288).

4.5 Summary

Analysing the spatial distribution of parameters within the Esk study catchment has revealed a number of areas of higher concentration, here termed 'concentration hot spots'. Concentrations of nitrate in a number of places in the catchment do have annual concentrations that are greater than the limit for freshwater pearl mussels that Skinner *et al.* (2000) mention. Many of the parameters are related to one another strengthening the assertion that mechanisms such as chemical weathering derive anions/cations from locally variable geologies. Greater variability in nitrate concentration was found in the sub-catchments with smaller catchment areas than sites with larger catchment areas which allowed tributaries to be highlighted as areas of higher concentration. Finally, the relationship between annual nitrate concentrations and upstream land cover percentages was investigated resulting in the relationship that higher percentages of arable land and improved pasture produce higher in-stream concentrations of nitrate (and higher percentages of moorland produce lower in-stream concentrations of nitrate.

5.0: Temporal variation in water quality in the River Esk

5.1 Introduction

This chapter investigates the temporal patterns in water quality found over the study period. It is vital to gain an understanding of how water quality changes temporally to develop our knowledge of whether the threats of hotspots identified in the previous chapter fluctuate based on aspects such as seasonality. To do this the water quality at each site over the 8-month sampling period is assessed in section 5.2. The influence of catchment size and land cover upon these records is explored in sections 5.3 and 5.4 respectively. Finally, changes in water quality at an hourly scale are analysed in section 5.5; both baseflow water quality (section 5.5.1) and the influence of increased discharge on water quality (section 5.5.2 onwards) are investigated.

5.2 Temporal variation

5.2.1 Monthly scale

The monthly data sets are displayed below for each site (anions on the left; cations on the right). A number of parameters register no value (below the limit of detection; see Chapter 3) including anions nitrite and phosphate and the cation ammonium. Fluoride and bromide values are close to the detection limits of the Dionex (0.01 and 0.02 mg l^{-1} respectively) and are very low (typically <0.1 mg l^{-1}) so trends are not distinguishable, however spatial catchment trends have been previously discussed (Chapter 4). All other variables provide visible trends that are discussed in depth here.

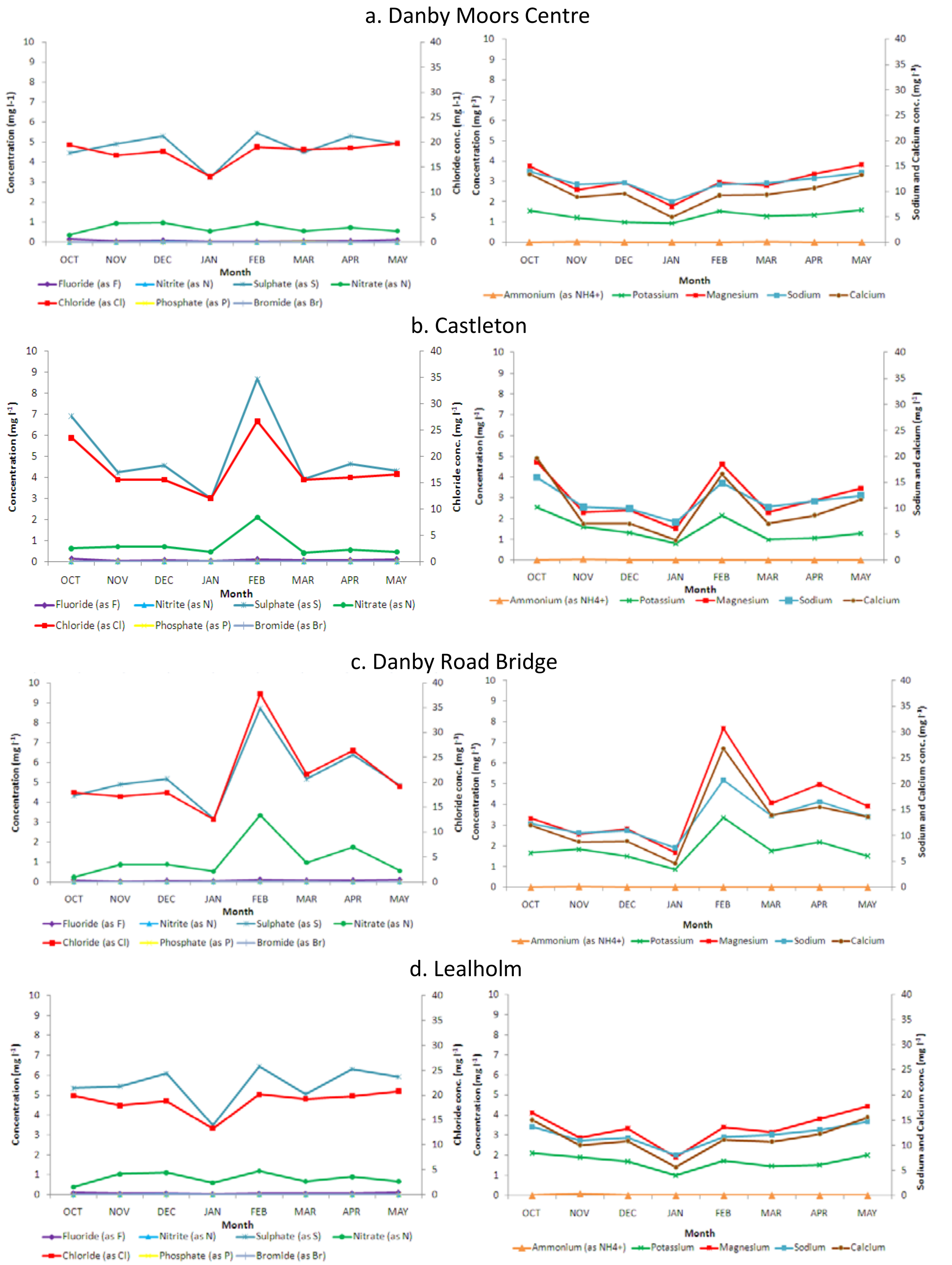
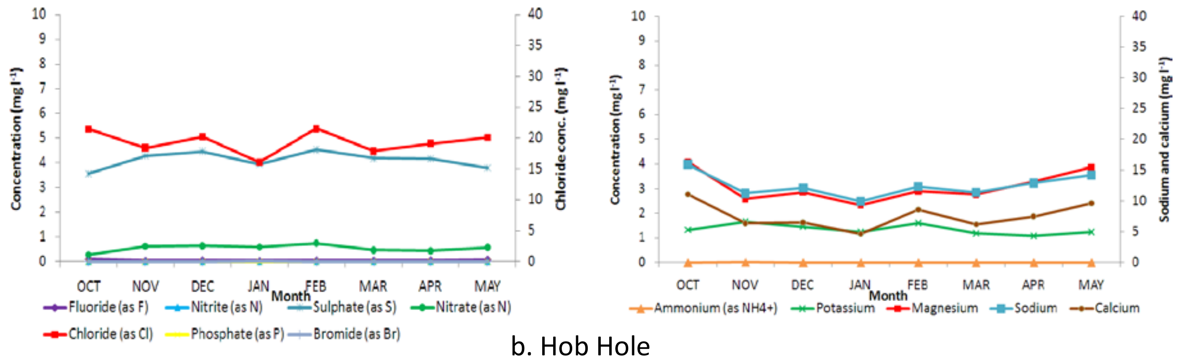


Figure 5.1: Temporal variation in anions (left) and cations (right) over the sampling period (Oct-May) at sites on the Esk at a. Danby Moors Centre; b. Castleton; c. Danby Road Bridge and; d. Lealholm

Figure 5.1 demonstrates the seasonal fluctuations in chemical parameters at selected sites on the main stem of the Esk over the 8-month study period; graphs that typify the trends and concentrations at other sites have been selected. At all main stem sites, the presence of ammonium, nitrite and phosphorus is negligible. The graphs in 5.1a (Esk at Danby Moors Centre) illustrate similar trends and concentrations to those at the Esk at Six Arches with consistent anion/cation levels apart from a decrease in concentrations in January of all components; thus coinciding with the impact of snowmelt in the system which may cause dilution at a catchment-wide scale. Figures 5.1b and 5.1c display flashy trends in concentration with concentrations falling from October to January which indicates the dilution of effect of increased precipitation through the autumn and winter months. The high concentrations at Danby Road Bridge may be due to the influence of the Toad Beck and the adjacent land cover which is primarily improved pasture. The Castleton site responds in the same manner which may be as a result of the cumulative input of headwater tributaries and the immediate impact of lowland land cover on the main stem. However, it is complex to deduce and speculate about controls on the signal here as the site receives inputs from Commondale Beck, Hob Hole, Westerdale Beck and Tower Beck. Finally, the Lealholm site (5.1d) presents a similar trend to that at Houlsyke, Glaisdale, Egton Bridge and Grosmont; this can therefore be inferred to be the typical main river concentration trends and concentrations once the system has reached equilibrium.

a. Commondale Beck: upstream



b. Hob Hole

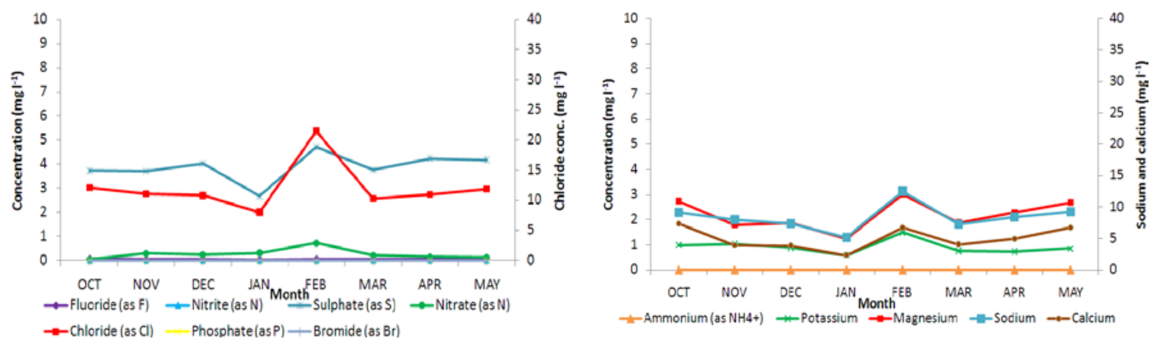
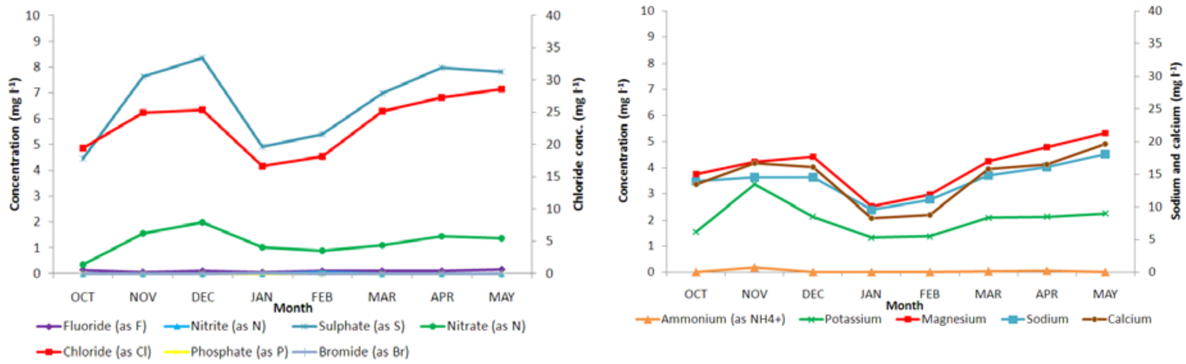
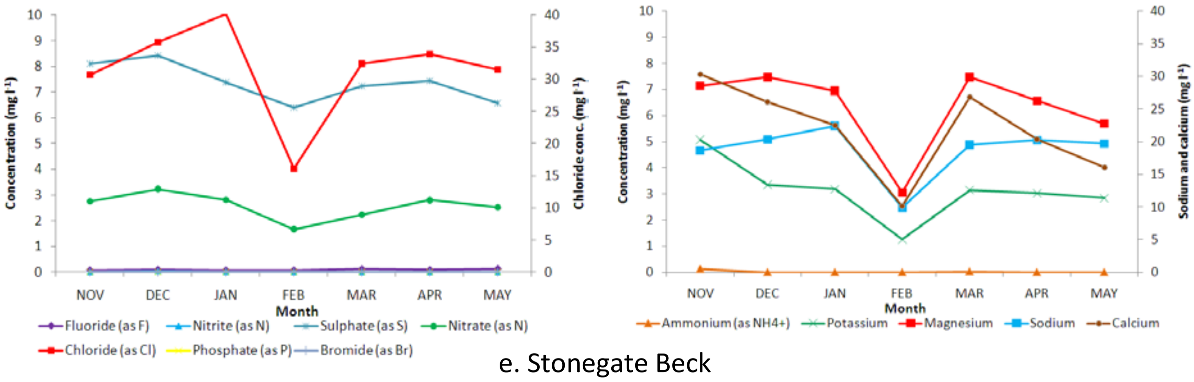


Figure 5.2 (part 1): Temporal variation in anions (left) and cations (right) over the sampling period (Oct- May) at sites on the Esk tributaries at a. Commondale Beck (upstream) and; b. Hob Hole

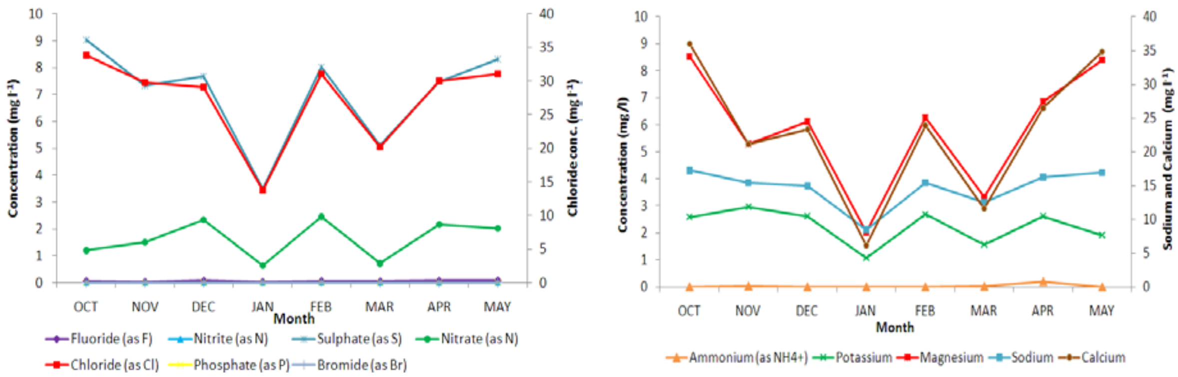
c. Danby Beck



d. Toad Beck



e. Stonegate Beck



f. Glaisdale Beck

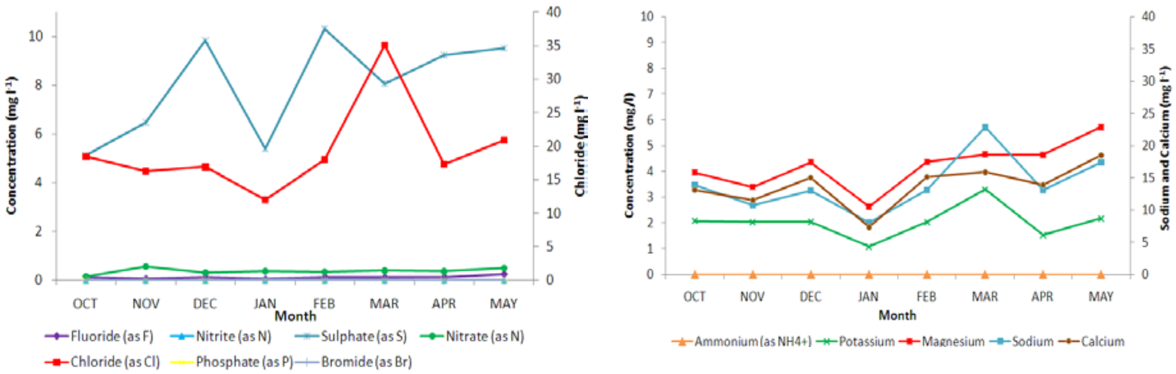


Figure 5.2 (part 2): Temporal variation in anions (left) and cations (right)- at sites on the Esk tributaries at c. Danby Beck; d. Toad Beck; e. Stonegate Beck and; f. Glaisdale Beck

Figure 5.2 presents the same data for selected tributaries to the Esk. Similar to all sites on the main river ammonium, nitrite and phosphate were not detectable (for detection limits see Chapter 3). Secondly, concentrations of both bromide and fluoride were minimal in the system. Also, most tributaries display increases in all anions/cations at the end of the sampling period which suggests the system is settling to its summer baseflow, and thus the dilution effect is decreased.

Commondale Beck (upstream; Figure 5.2a) reveals similar trends and concentrations to those resulting from Commondale Beck Box Hall (downstream); this is because the same source areas influence the chemical composition of the Commondale Beck system. Commondale Beck drains the northern portion of the headwater zone into the Esk by Castleton and, in contrast to the other headwater systems that drain the southern area of the headwater catchments (Tower Beck, Hob Hole and Westerdale Beck), has higher concentrations which may indicate a difference in land management/practices. These southern headwater catchments (listed above) are all nutrient-poor and recorded trends and concentrations comparable to those in Figure 5.2b (Hob Hole). This may be due to the topography and hydrological connectivity influencing the received rainfall to dilute the concentrations of these parameters; this effect may be more significant here as the source areas of these tributaries are located in the areas of highest annual rainfall figures within the catchment (Environment Agency, 2005).

Danby Beck, Toad Beck and Stonegate Beck (Figure 5.2c/d/e respectively) are the tributaries with the highest concentrations and most variable trends. Concentrations are often more than double those recorded at headwater tributary sites such as Westerdale Beck and Hob Hole. This indication of a greater nutrient richness is often a sign of differences within the contributing source areas, particularly the land cover influence, which will be explored in greater detail later. The nitrate levels in these tributaries, which are of particular interest with regard to the freshwater pearl mussel, are found to be the most elevated compared to other monitoring sites. Toad Beck for example fluctuates from a minimum of 1.7 mg l^{-1} in February to a maximum of 3.2 mg l^{-1} in December, and therefore all values are over the stated 1.0 mg l^{-1} freshwater pearl mussel tolerance level (Skinner *et al.*, 2003). A point of contention is the extent to switch sub-catchments and tributaries with concentrations of this level affect the levels in the main stem.

Glaisdale Beck (Figure 5.2f) demonstrates similar trends to Great Fryup Beck in terms of both concentration and parameter trends. The chloride-sulphate trends differ significantly which is unlike the trends found in other tributaries and main stem sites. It can be hypothesised that in these lowland tributary systems that the soils are more sulphate-rich and therefore larger concentrations can be mobilised by water moving to the channels.

5.2.2 Longer-term record

At a number of sites it is possible to generate a longer-term record of these chemical parameters via the use of secondary data (from Bracken, 2009). Due to the complex chemistry within landscapes and influence on habitat/freshwater pearl mussels, only the data for potassium and nitrate records are examined. Of the nine sites monitored by Bracken (2009), Danby Beck and Stonegate Beck have been selected for analysis as they have been identified as regions with higher concentrations in the previous section and have relatively high seasonal variability. Figure 5.3 demonstrates the fluctuations in anions and cations at these sites over approximately 2 years:

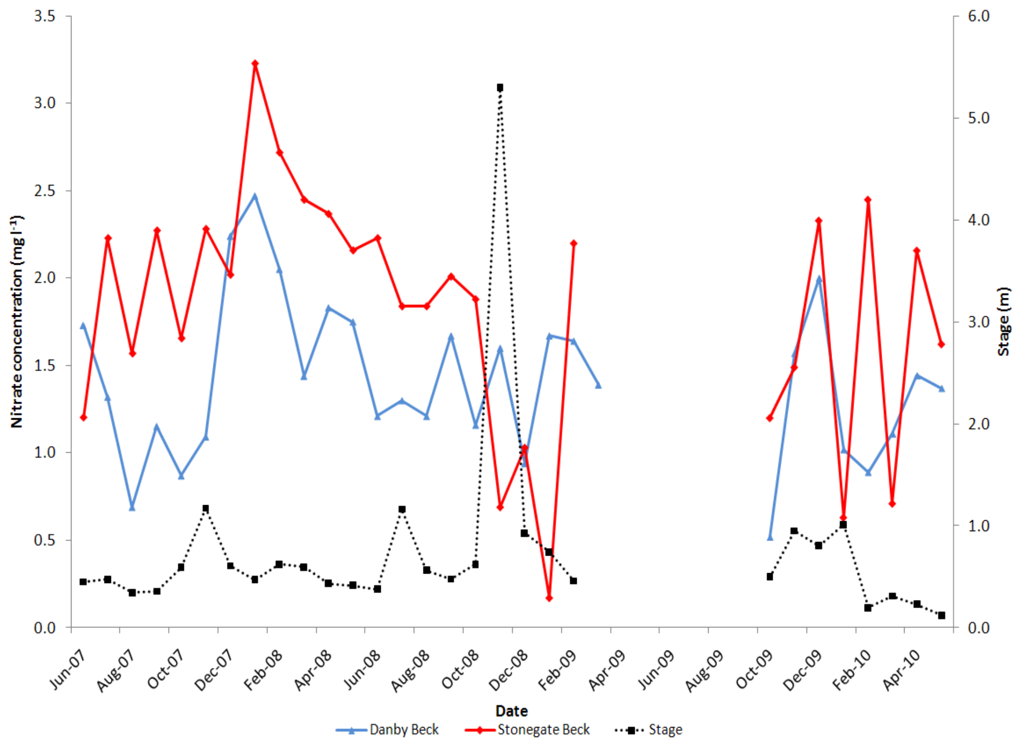


Figure 5.3: Nitrate concentrations at Danby Beck and Stonegate Beck and daily average stage (Danby logger record)

The longer-term records of nitrate at Danby Beck and Stonegate Beck indicate varying seasonal trends. In 2007 it appears that nitrate concentrations increased from summer to the winter months whereas in 2008 the opposite pattern exists in at Stonegate Beck and consistent concentrations appear at Danby Beck throughout the year. At first it could be questioned that this section of the record points towards decreasing nitrate concentrations in Stonegate Beck which would be a positive sign for the freshwater pearl mussel population in the Esk as the majority of concentrations recorded are over the 1.0 mg l^{-1} limit suggested by Skinner *et al* (2003). However, it is more likely that this demonstrates an element of dilution created by high stage events such as that in November 2008; furthermore a decline in nitrate concentrations at Stonegate Beck can be dismissed by the re-elevated concentrations monitored during October 2009 to May 2010. Therefore it can be suggested that these trends add weight to the proposition that nitrate interacts with the landscape and riverine habitat in a complex manner affected especially by hydrological connectivity, human land use (e.g. fertiliser application/grassland ploughing) and climatic variability.

Secondly, despite the two sites being relatively far apart in the study area, there is a similar pattern of increase/decrease in the captured nitrate concentrations. For example, concentrations increase at both sites from summer 2007 to both peak in January 2008. This allows for the suggestion of a catchment-scale response in nitrate concentrations to processes (both natural and human influenced). Therefore, it can be assumed that similar processes are in operation in both sub-catchments. However there are also differences in trends, for example, in February 2010 the concentration at Danby Beck continues to decrease to from 1.0 mg l^{-1} in January to 0.9 mg l^{-1} whereas at Stonegate Beck concentrations increase from 0.6 mg l^{-1} in January to 2.5 mg l^{-1} in February. This indicates that catchment complexity does influence the concentration monitored at any individual site.

The daily average stage record is perhaps of little use as nitrate can gradually enter the river system in what Kirchner (2003) terms 'old water' that is pushed through the system (as through flow) which mobilises nitrate in the soil. This therefore justifies the use of autosamplers to sample on an hourly basis which allows the water quality to be monitored over the duration of an event allowing the influence of stage on nitrate to be assessed (see section 5.5.4). On the other hand, it should be acknowledged that these data are from the logger at Esk at Danby and therefore will have a different hydrological signal to those in Danby Beck and Stonegate Beck. Despite this, the stage signal appears to demonstrate similar trends to those found in both sites especially at Danby Beck. However, this is a weak association as the samples are only one-off point samples thus to illustrate the impact of stage on nitrate data must be sampled at a higher resolution.

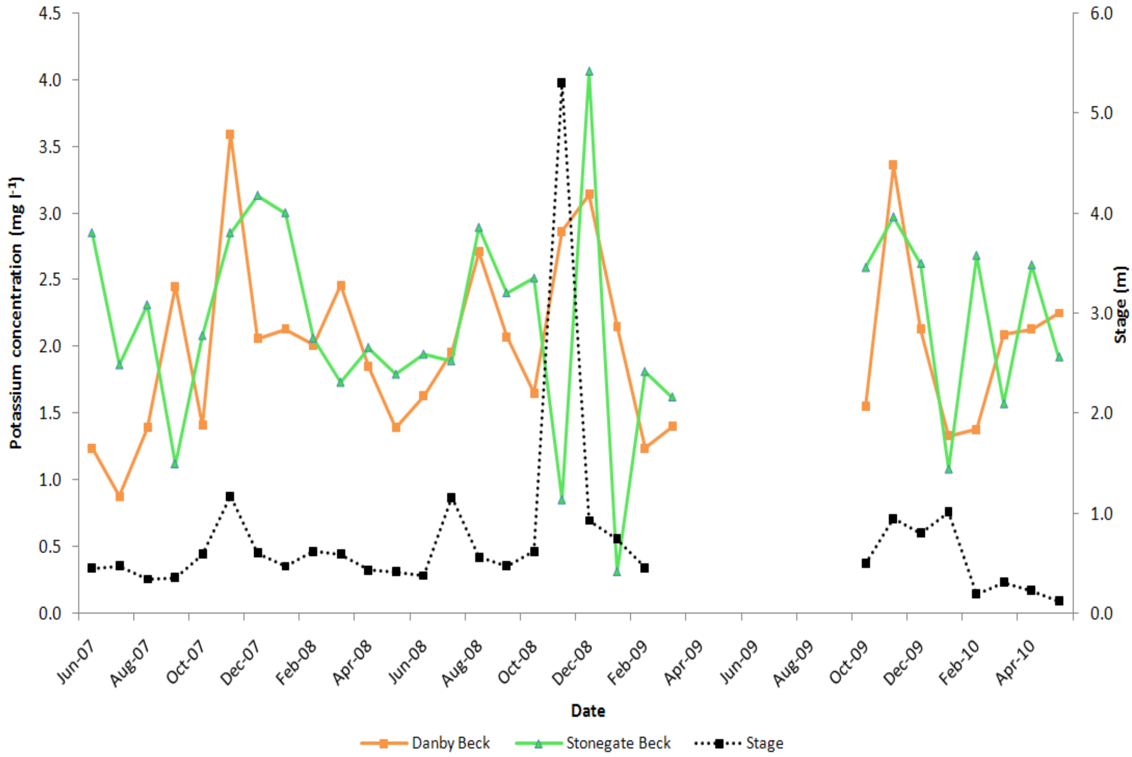


Figure 5.4: Potassium concentrations at Danby Beck and Stonegate Beck and daily average stage (Danby logger record)

Similar to the longer-term records of nitrate concentrations, the potassium records demonstrate comparable trends at Danby Beck and Stonegate Beck (see Figure 5.4). For example, in November 2007, August 2008 and November 2009 there are increases in potassium concentrations at both sites. This again emphasises catchment-wide responses to natural and anthropogenic processes that influence the Esk's river water chemistry. These three highlighted examples can be mapped onto an increase in stage; this agrees with the typical trend that potassium concentrations increase with stage (Stott and Burt, 1997). However, this is not always the case as the high stage event sampled in November 2008 indicates a decrease in concentration at Stonegate Beck but an increase at Danby Beck. This denotes the fact that different areas of the catchment will respond to different conditions in varying ways. Nevertheless, the Stonegate Beck potassium concentration rapidly increases to the maximum recorded value in this sub-catchment (4.1 mg l^{-1}) in the following month (December 2008), denoting a possible delay in the mobilisation of potassium soil sources. It is worth noting that this 3-year record is valuable however does not pick up the impact of extreme events that affect the catchment periodically as the climate dictates. Therefore a network that addresses sampling in extreme events, as discussed below, would be helpful to this end.

5.2.3 Other parameters

A number of parameters measured with the YSI multi-parameter probe are displayed below. Data are displayed for pH, conductivity and dissolved oxygen as these parameters provide information on the quality of habitat and allow for inference of catchment characteristics and therefore mechanisms (see Figure 5.5). The sites have been ordered on the x axis by the catchment area upstream of the sample point.

The pH is a key parameter within any water system as it has notable effect on both biological and chemical processes (Chapman and Kimstach, 1996). The pH measurements indicate the activity of hydrogen ions (H^+) and are controlled by mechanisms that create or use H^+ (Hem, 1985). There appears to be little variability within the values monitored. All records are between 6.0 and 8.5 which is the range expected in most natural waters (Hem, 1985; Chapman and Kimstach, 1996). However the rationale here relates to freshwater pearl mussels, a species that require a higher quality of water for survival (Moorkens, 2000). Skinner *et al.* (2003) state that freshwater pearl mussels require waters of pH 7.5 or less. Degerman *et al.* (2009) cite Söderberg *et al.* (2008a) as stating a lower limit of pH as 6.1-6.3. There are a number of sites and months where this boundary is exceeded; for example, at the Esk at Danby Road Bridge 3 of the 4 months assessed for pH with the YSI probe resulted in pH levels greater than 7.5 (7.6, 7.7 and 7.7). This may be an influence of the nearby land cover; indeed the Toad Beck sub-catchment, which joins the Esk adjacent to the Danby Road Bridge site, has a high proportion of improved pasture and arable land.

All values in March, April and May have a pH greater than 7.0 and therefore are considered to be alkaline (Ward and Robinson, 2000). On the other hand, those recorded in February are lower than all other values; this erratic pattern is comparable to anion/cation patterns found for February. A possible factor that may have caused this result may be a greater discharge via the addition of snowmelt to the system which will have affected the pH equilibrium as the availability of H^+ ions was increased and hence the catchment exhibited lower pH values (more acidic). In particular the pH at Hob Hole Beck (6.0) stands out relative to majority of the rest of the catchment flush. This area is known for acid flushes (Bargh, personal communication) and although it is only mildly acidic this may explain the difference in relation to elsewhere in the catchment. The reactions occurring are reversible thus forming a dynamic equilibrium that operates in the river network (Ward and Robinson, 2000). Therefore, with a larger than average input into a system, as in February, and this dynamic equilibrium in operation, processes will be triggered that cause a shift from typical conditions.

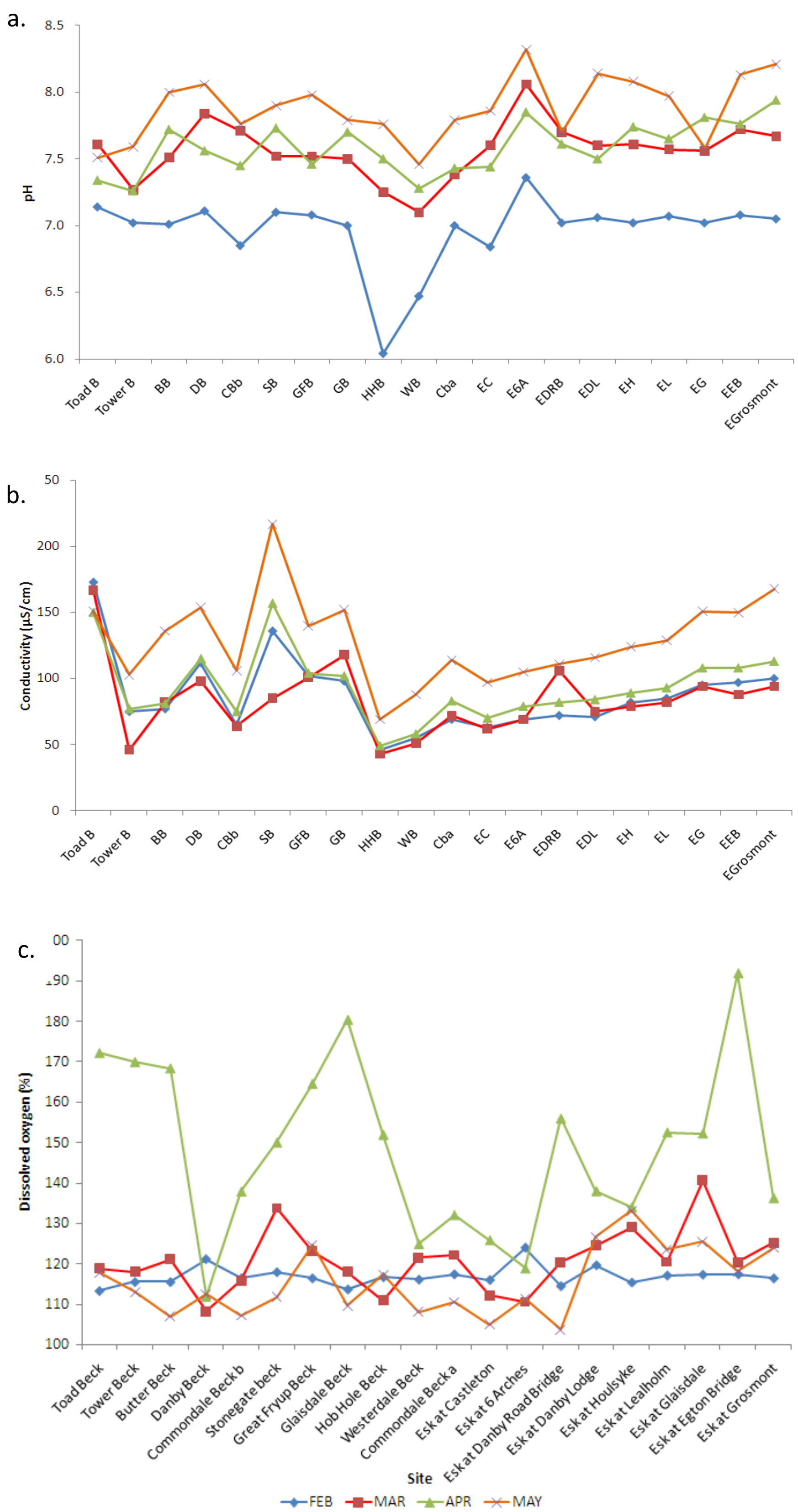


Figure 5.5: a. pH, b. Conductivity and c. Dissolved oxygen at all sites from February 2010-May 2010

Conductivity is an indicator of the ability of the river water to conduct an electric current (Hem, 1985). It is particularly affected by dissolved solids; therefore, it relates to how well minerals dissociate into their ionic constituents (Chapman and Kimstach, 1996). Firstly, February, March and April all exhibit similar trends and values at all sites that were monitored (see Figure 5.5b). It appears that the conductivity values are both highest and most variable in the Esk tributaries. Stonegate Beck represents the highest recorded conductivity figures in the catchment (averaging 149 µS cm^{-1}). This may be due to the geology in this sub-catchment of the Esk. May illustrates the same trend as found in the other analysed months, however values are a degree larger at each site; this may be an issue with the calibration of the equipment. This is probably an indicator of the higher summer conductance levels where low flows result in reduced dilution of the ions that create the potential current. With increasing distance down the main stem, conductivity values gradually increase. This is likely to be due to the combined influence of an increasing urban environment and thus pollution sources; a cumulatively increasing contribution area plus the cumulative contribution from eroded materials downstream.

Skinner *et al.* (2003:11) state that dissolved oxygen (DO) is ‘undoubtedly of importance’ to the pearl mussel species’ longevity and therefore it is important to assess how this parameter varies in the Esk. In Chapter 4, a number of areas were noted as having high DO values and thus it is useful to see if these annual trends are mirrored throughout the sampling period (monthly scale). Figure 5.5c displays no obvious consistent pattern of high DO values at any particular site month-by-month and values instead fluctuate with non-uniformity independent to catchment area (unlike other parameters e.g. nitrate (Figure 5.6) and conductivity (Figure 5.5b)). The dissolved oxygen temporal record (Figure 5.5c) displays a consistent range of values in February, March and May; with values fluctuating from ~100 % - ~130 %. Variation in DO can occur seasonally; however, fluctuations can appear over 24-hour periods. For example, increased temperature increases the solubility of oxygen and thus increases DO (Chapman and Kimstach, 1996). It can be postulated that this fact can explain the between-site variability present in the record as water was analysed over a period of typically 6 hours therefore, for example, allowing the sun to warm the water over the course of the sample period. Nonetheless in April the trend is more varied and values differ to a greater extent compared to the other months with minimum readings around 110-120 % and maximum readings greater than 170-180 %. Oxygen content within rivers can vary via factors such as temperature, salinity, turbulence, photosynthetic rate of flora and atmospheric pressure (Chapman and Kimstach, 1996). Therefore, it can be speculated that this April result is due to climatic differences, variation in flow and growth rate. However, it must be noted that these DO levels are recorded in the water column where adult pearl mussels exist and therefore cannot explicitly be related to juvenile pearl mussels that live interstitially and are therefore not accessing water directly from the water column (Skinner *et al.*, 2003). As Skinner *et al.* (2003) highlight, interstitial environment assessment is required to add to the minimal research on this area (e.g. Buddensiek *et al.*, 1993).

5.3 Catchment size influence at a temporal scale

Figure 5.6 demonstrates and strengthens the relationship presented in Chapter 4 (section 4.3). The temporal influence over this catchment area driver is investigated for nitrate as it is a key nutrient with influence upon water quality (Heathwaite *et al.*, 1996). Main stem concentrations in over 50% of the months sampled threaten and often pass the 1 mg l^{-1} level quoted by Skinner *et al.* (2003). Therefore, it is important to examine how this parameter influences nitrate concentration on a monthly scale.

Two clusters can again be distinguished within the data (see May diagram in Figure 5.6), one with higher variability and concentrations in the smaller contributing areas (termed cluster 1 here) and another with lower variability and concentrations in the larger contributing areas (termed cluster 2). This cluster pattern appears to be maintained throughout the 8-month sample period. October has a slightly different pattern as not all sites were sampled, because it was a preliminary sample run; concentrations recorded in this run were all below average. In February on the other hand, whilst clusters 1 and 2 are still evident, greater variation and spread of concentrations is displayed; here Toad Beck exhibits its lowest recorded concentration (1.7 mg l^{-1}) and a number of main stem sites have unusually high concentrations (Esk at Castleton, 2.1 mg l^{-1} and Esk at Danby Road Bridge, 3.3 mg l^{-1}). This is emphasised by the fact that concentrations in the two months either side, January and March have relatively low concentrations with all values (apart from the consistently high Toad Beck and Tower Beck in March) are less than 1.0 mg l^{-1}. Yet in February 55 % of the sites have nitrate concentrations greater than 1.0 mg l^{-1}. Interestingly, of the 55 % with of sites with concentrations over 1.0 mg l^{-1} sites, cluster 2 (sample points on the main stem) dominates.

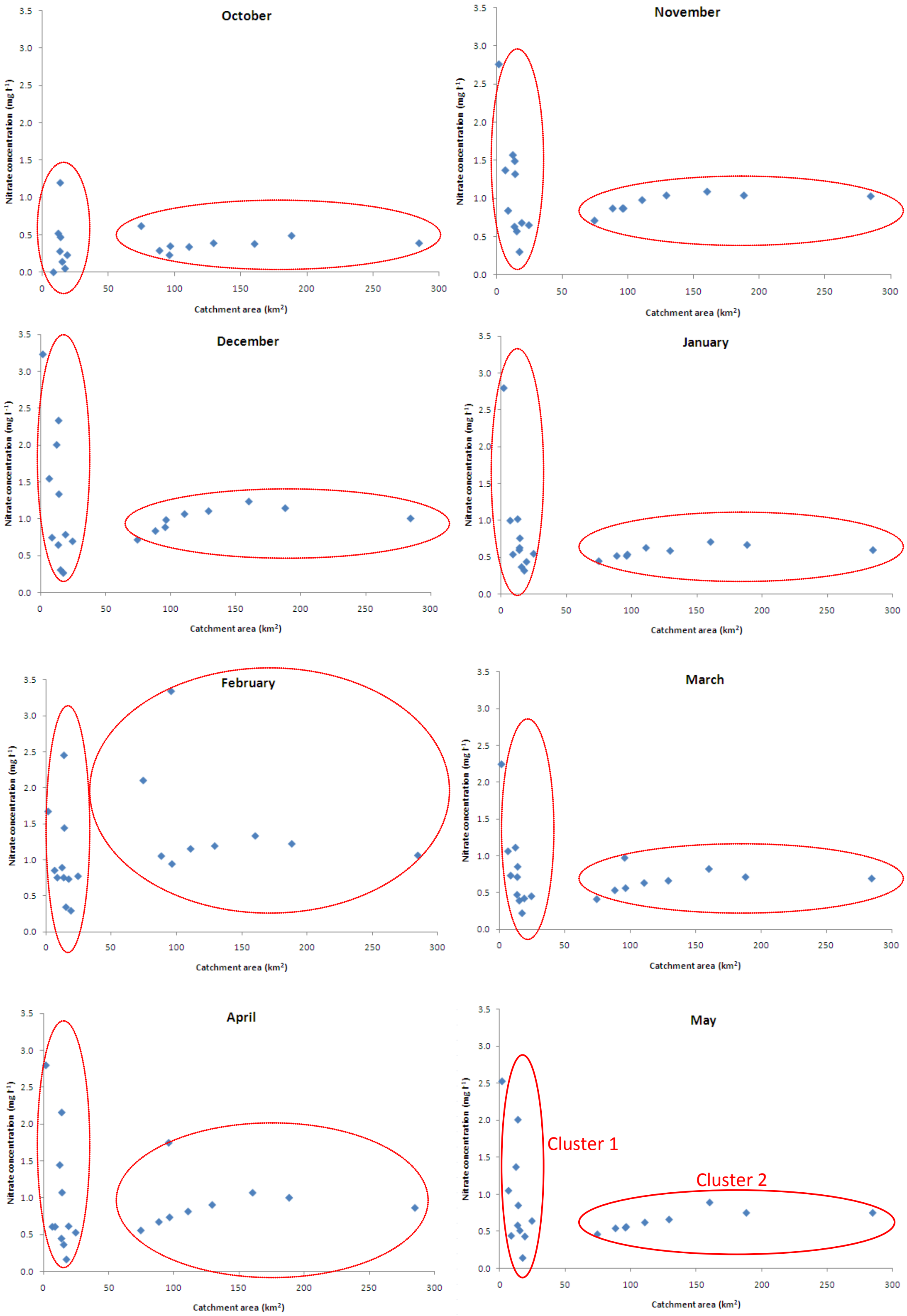


Figure 5.6: Nitrate concentrations from 20 sites plotted against catchment area/contributing area for October 2009- May 2010. Clusters (1 and 2) identified on May diagram

Essentially the points that make up cluster 1 are tributary sites (with the smaller catchment areas- < 50 km^2) and the points that make up cluster 2 are main stem sites (with larger catchment areas > 50 km^2). Table 5.1 demonstrates the mean and standard deviation of each cluster (in each month) to give a numerical impression of the variability the results express.

Table 5.1 Mean and standard deviation of clusters 1 and 2 in the nitrate concentration/catchment area trend from October 2009 – May 2010

	Cluster 1		Cluster 2	
Month	Mean (mg l^{-1})	Standard Deviation	Mean (mg l^{-1})	Standard Deviation
October	0.41	0.39	0.39	0.11
November	1.11	0.70	0.94	0.12
December	1.26	0.94	0.99	0.16
January	0.82	0.69	0.58	0.08
February	0.99	0.63	1.49	0.77
March	0.79	0.56	0.66	0.16
April	0.98	0.83	0.93	0.35
May	0.96	0.74	0.64	0.13

Table 5.1 allows for cluster 1 and cluster 2 (C1 and C2 respectively) to be compared. The mean values of C1 and C2 in each month are not much different e.g. April (C1: 0.98, C2: 0.93). It seems that usually the C1 mean is higher than the C2 mean yet in February this was reversed (possibly due to snowmelt discharge additions). However, the standard deviations of the clusters in each month illustrate the variation around the mean. The standard deviations of C1 data are all much higher relative to those in C2. Again, February stands out as an anomalous month that does not demonstrate this trend, yet generally these data exhibit that in the main stem sites the concentrations are relatively consistent and the sub-catchments (or tributaries) demonstrate that there is a greater variation in concentration between sub-catchments. Therefore, these data strengthen the point of greater variability in smaller catchments and lower variability in larger catchments

Catchment area can therefore dictate a measure of control upon a parameter concentration at a particular point in a river system. This measure of control is complex and not as simple as just exposure time within the catchment. Characteristics such as discharge, drainage density, hyporheic processes and connectivity interact with other factors such as land management, land cover and geology to determine the water quality. Therefore, the influence of catchment dynamics and characteristics such as quickflow-dominated or baseflow-dominated, nutrient rich or nutrient poor, geology type, poorly-connected or well-connected must be considered alongside catchment area when assessing reasons for catchment concentration patterns. However, it should be noted that it is problematic to compare catchments of different sizes due to complications of within-catchment variability that is typically greater in larger catchments (Burt and Pinay, 2005).

Chapter 4 discusses research by Burt and Pinay (2005) which illustrates that tributary catchments exhibit higher variability in nutrient flux compared to that in the entire river basin and data from monthly runs agrees with this observation. Figure 5.6 strengthens this argument because this pattern of higher variability in the tributary sub-catchments of the Esk and lower variability in the main stem of the Esk is exhibited at a monthly scale (as well as an annual timeframe). Strayer *et al.* (2003) suggest that this indicates a low signal-noise ratio in large catchments and higher in smaller catchments. For example, changes in land cover are dampened out by the higher discharge in the system, for example, at Grosmont the signal and impact of catchment characteristics or pollution events are reduced whereas in Toad Beck or Westerdale Beck changes in the system are more easily identified. Caraco *et al.* (2003) noted, in terms of nitrate export, that the factors that drive variability may be operating more strongly in smaller catchments than in larger catchments therefore making such parameters harder to estimate in catchments with lower upstream areas; this agrees with the data exhibited in Figure 5.6 that the drivers of variability that exist within catchments such as Toad Beck, Stonegate Beck, Westerdale Beck and Hob Hole can operate to a greater extent compared to those with larger upstream areas, the main stem sites e.g. Esk at Lealholm and Esk at Houlsyke.

It appears that the trend displayed by Burt and Pinay (2005) in different catchment systems of greater variability in smaller catchments and reduced variability in larger catchments is evident at a monthly scale as well as at an annual level (see Chapter 4). There is the notable fluctuation of the typical pattern in February but this may be due to the influence of snowmelt following the period of snowfall. Yet there is greater variability between sub-catchments site concentrations than between main stem site concentrations.

5.4 The temporal influence of land cover

The modification of the landscape affects natural processes that influence the water quality (Baker, 2003), for example, irrigation uses reducing river discharge. Land use is noted to be the ‘primary driving force’ of water quality at a catchment scale (Chang, 2008: 3299). Therefore, it is vital to assess how the monthly changes in water quality parameters relate to land use (and thus land cover) within the Esk. Chang (2008) found temporal (and spatial) variability in water quality parameters to be linked with land development (and natural processes). It is worth noting that whilst land cover may not change much over time it is possible that land use may well be altered more frequently. For example, crop rotation and the cycling of management techniques provide land use changes yet the land cover remains arable land during these periods. Rothwell *et al.* (2010) state that knowledge of catchment water quality and catchment characteristics provides a firm base to estimate how future changes in land cover and land use will affect catchment water quality. In light of this, as land use and even land cover modification occurs in the Esk catchment, it will be important to generate an understanding of how this may influence water quality over time. Chapter 4 highlighted the patterns demonstrated by nitrate using annual statistics and here the relationships between parameters and land cover changes over the 8 month sampling period are investigated. This was done by finding the Pearson correlation coefficient r-values between the land cover percentages in each sub-catchment (contributing upstream area) and the concentrations generated each month (October 2009-May 2010).

Nitrate was highlighted to be one of the most significant pollutants in the Esk catchment study area (see Chapter 4). Secondly, scientific understanding of the impact of land use and how it modifies river nitrate levels is not satisfactory (Poor and McDonnell, 2007). Therefore, it is necessary to examine variations in the relationship between land use (and thus land cover) and monthly concentrations of nitrate, testing whether the nitrate concentration varies consistently with land cover. The significance of the relationships will indicate the level of control a land type has upon the nitrate concentration. The following table presents Pearson r-values to represent the correlation between monthly nitrate concentrations and the three main land cover categories in the study area of the Esk catchment:

Table 5.2: Pearson's correlation coefficient r-values for the relationship between nitrate concentration and land cover types (arable, improved pasture and moorland), at 18 degrees of freedom (as n=20) 95% significance level= +/-0.44 (*); 99% significance level= +/-0.56(**); 99.9% significance level= +/-0.68 (***)

Month	Arable	Improved	Moorland
October	0.74^{***}	0.49^{*}	-0.20
November	0.77^{***}	0.87^{***}	-0.70^{***}
December	0.80^{***}	0.80^{***}	-0.61^{**}
January	0.61^{**}	0.75^{***}	-0.59^{**}
February	0.30	0.18	-0.03
March	0.62^{**}	0.80^{***}	-0.66^{**}
April	0.79^{***}	0.69^{***}	-0.52^{*}
May	0.88^{***}	0.80^{***}	-0.56^{**}

There is a significant relationship (at the 95% confidence level) between the nitrate concentration and both the arable and improved pasture land cover in the contributing area upstream of each site, in all months excluding February. Previous research has found strong correlation with between chemical determinants and land cover typologies; similarly Jarvie *et al.* (2002) discovered strong associations between the proportion of arable land (and catchment urbanisation) and river nutrient concentrations in the Humber catchment.

February notably stands out with low correlation coefficients; this indicates that in February other factors, such as climatic inputs or antecedent conditions prior to the sampling period, are most probably the reason for the nitrate concentration. It seems that the heavy snow cover in January and February and the following snowmelt addition into the network in this period was a large influence upon the nitrate concentrations. Climatic conditions, as well as land use, are acknowledged to be associated with temporal variation in water quality (e.g. Chang, 2008). The correlation coefficients for a number of other parameters are displayed in Tables 5.3-5.8. Parameters analysed here are datasets with measurable concentrations unlike parameters that were too small to detect such as ammonium.

Tables 5.2-5.7 demonstrate a similar pattern to that in 5.1, signifying the likelihood that land cover in the Esk (the balance between arable, improved and moorland land covers) is a significant aspect influencing the properties of water quality within the Esk and its tributaries. It appears that moorland has the opposite effect on the system compared to arable and improved pasture. Many of the correlation coefficients are greater than 0.68 and are thus indicative of significant relationships at a monthly level between chemical parameters and land cover types in the Esk catchment and so providing further evidence of interactions between the two variables (Burt and Pinay, 2005). The relationship between all six parameters analysed and the three main land covers in February (Tables 5.3-5.8) exhibit insignificant relationships further strengthening the assertion made above (with regard to nitrate and land cover) that here natural processes (e.g. climatic conditions- snowmelt via higher temperatures adding to river discharge).

In summary, this evidence substantiates research that has uncovered ‘reasonable correlations between the proportions of land cover types and nutrient export’ (Burt and Pinay, 2005:298). However, it must be noted that all catchments are inherently complex with spatial and temporal variations in natural processes and land use (Chang, 2008) and therefore nutrient variables display ‘marked differences depending on the location and the season’ (Perona *et al*., 1999:75). Yet persisting with this route of investigation is useful, especially when addressing diffuse pollution which is problematic to measure. This will add depth to the understanding of the land use/land cover-water quality relationship and help to create a means to estimate diffuse pollution in river systems (Baker, 2003).

Tables 5.3- 5.8: Pearson's correlation coefficient r-values for the relationship between parameter concentration and land cover types (arable, improved pasture and moorland), n = 20 thus at 18 degrees of freedom when 95% significance level= +/-0.44(*); 99% significance level= +/-0.56 (**); 99.9% significance level= +/-0.68 (***)

Month	Arable	Improved	Moorland
Oct	0.63**	0.65**	-0.42
Nov	0.82***	0.87***	-0.68***
Dec	0.94***	0.83***	-0.58**
Jan	0.67**	0.75***	-0.53*
Feb	0.25	0.04	0.09
Mar	0.69***	0.76***	-0.64**
Apr	0.87***	0.73***	-0.54*
May	0.81***	0.81***	-0.65**

Table 5.3: Potassium

Month	Arable	Improved	Moorland
Oct	0.82***	0.58**	-0.24
Nov	0.92***	0.87***	-0.65**
Dec	0.97***	0.86***	-0.63**
Jan	0.66**	0.76***	-0.58**
Feb	0.31	0.12	-0.01
Mar	0.72***	0.84***	-0.70***
Apr	0.92***	0.72***	-0.50*
May	0.87***	0.63**	-0.42

Table 5.4: Magnesium

Month	Arable	Improved	Moorland
Oct	0.80***	0.57*	-0.28
Nov	0.91***	0.87***	-0.67**
Dec	0.97***	0.86***	-0.65**
Jan	0.70***	0.81***	-0.64**
Feb	0.38	0.17	-0.04
Mar	0.73***	0.85***	-0.74***
Apr	0.90***	0.66**	-0.47*
May	0.76***	0.49*	-0.33

Table 5.5: Calcium

Month	Arable	Improved	Moorland
Oct	0.78***	0.42	-0.01
Nov	0.90***	0.71***	-0.42
Dec	0.88***	0.70***	0.-40
Jan	0.60**	0.67**	-0.44*
Feb	0.16	-0.12	0.27
Mar	0.67**	0.67**	-0.50*
Apr	0.80***	0.58**	-0.33
May	0.89***	0.64**	-0.35

Table 5.6: Chloride

Month	Arable	Improved	Moorland
Oct	0.66**	0.41	-0.05
Nov	0.86***	0.75***	-0.50*
Dec	0.86***	0.73***	-0.47*
Jan	0.60***	0.68***	-0.44*
Feb	0.12	-0.11	0.23
Mar	0.62**	0.65**	-0.51*
Apr	0.77***	0.60**	-0.38
May	0.84***	0.66**	-0.46*

Table 5.7: Sodium

Month	Arable	Improved	Moorland
Oct	0.70***	0.71***	-0.48*
Nov	0.85***	0.91***	-0.77***
Dec	0.75***	0.85***	-0.75***
Jan	0.65**	0.85***	-0.70***
Feb	0.38	0.40	-0.36
Mar	0.60**	0.84***	-0.78***
Apr	0.70***	0.73***	-0.69***
May	0.70***	0.73***	-0.67**

Table 5.8: Sulphate

5.5 Hourly scale: autosamplers

In addition to month-by-month data, three autosamplers were installed to allow for finer resolution observations and understanding of the water quality variation in the Esk. This is important for the freshwater pearl mussel as sudden inputs of nutrients or sediment to channel may be detrimental to a) the species itself and/or b) the species natural habitat. Both fluctuations at baseflow and stormflow are worth investigating to see how levels change at a finer temporal scale. Research has shown that changes in discharge can influence water quality. The autosampler network may capture flushing of sediment and nutrients like nitrate and potassium in periods of high discharge which may not be captured in the monthly sampling network. If shorter term changes in water quality parameters are present they are certainly worth monitoring as, even though they have a shorter duration, compared to baseflow levels they may have an impact on the species. Autosamplers can be utilised to interrogate both the baseflow river levels and stormflow river levels, and therefore are ideal to addressing how the changing nature of the discharge conditions influence the properties of the water and in turn the freshwater pearl mussel population.

5.5.1 Baseflow water quality

Autosamplers were operated in baseflow conditions to allow the anions and cations from the Esk during consistent base discharge periods to be analysed. Figure 5.7a displays data from 5/5/10 at Danby where the stage is at summer base levels with the stage level at the stilling well monitored to be ~14 cm. The diagram illustrates steady, consistent levels of the anions and cations with no fluctuations present. Figure 5.7b and c are from the same 24 hour period in February (18/2/10) as Grosmont and Lealholm respectively; again anion/cation parameters exhibit steady, consistent values over the sample period. However, there are a number of small fluctuations visible in both chloride and sodium at both Lealholm and Grosmont. Sodium chloride is a common compound; therefore, it is not surprising that both components display the same pattern (particularly at Lealholm). These minor fluctuations may indicate that the climatic conditions over the monitored period and/or prior to the monitored period were dictating the signal in the system and therefore the natural conditions were the cause for the fluctuations. Indeed, when assessing the stage record (for Grosmont) (see overview in Chapter 3) it can be observed that the Esk on 18/2/10 was returning to typical river level following a rainfall event that triggered a rise in stage to over 1 m. Therefore, a slight variation within these parameters is likely as the system re-adjusts to base levels of both flow and concentrations following this discharge event.

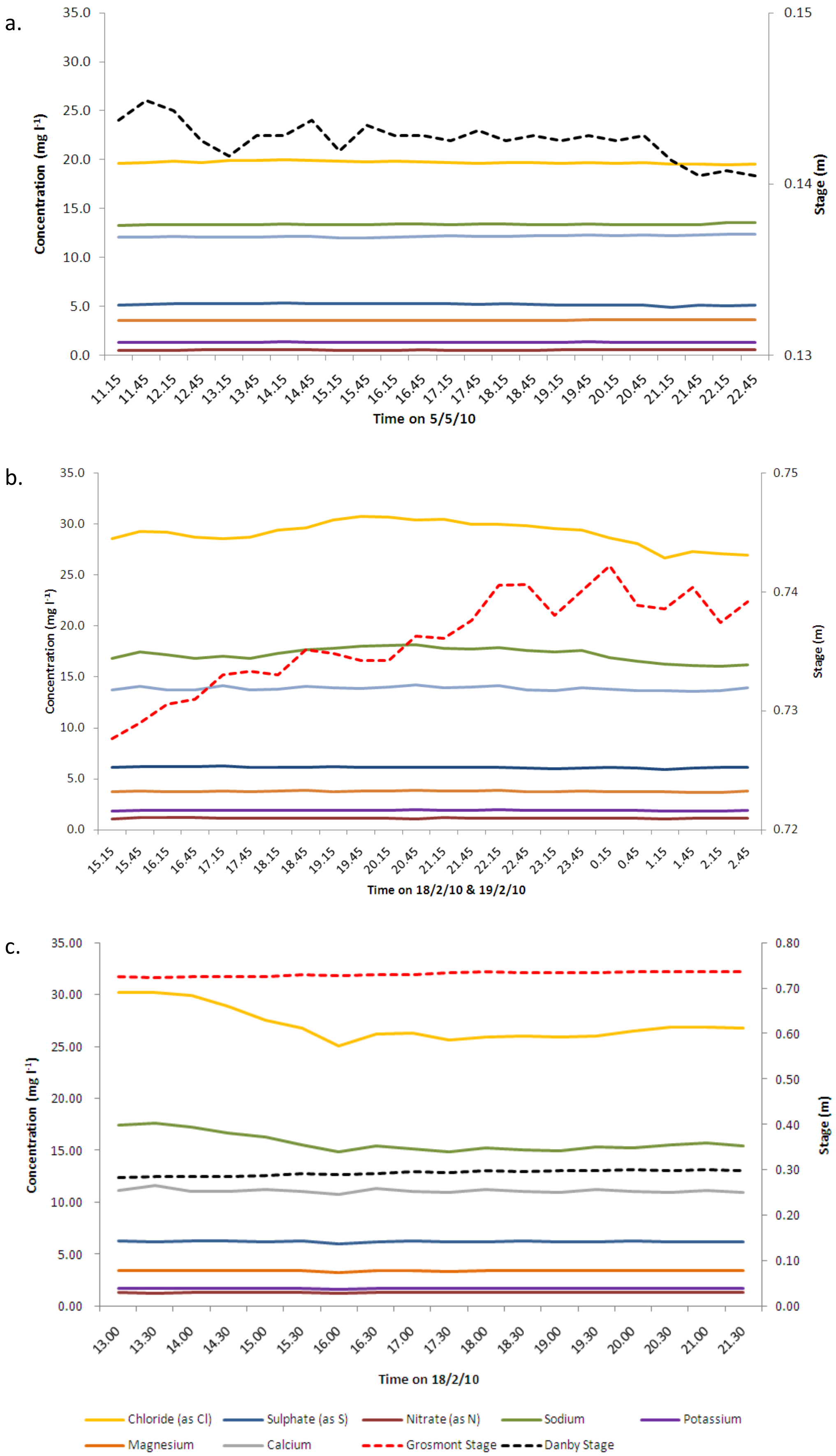


Figure 5.7: Selected anions and cations from (a) Danby (5/5/10); (b) Grosmont (18/2/10); and (c) Lealholm (18/2/10)

Despite being from different sites, it is interesting to note the difference between parameter levels between months. For example in February in the Esk at Lealholm and Grosmont chloride levels fluctuate ~25.0 -30.0 mg l^{-1}, whereas in May in the Esk at Danby they are consistently 19.5 - 20.0 mg l^{-1}. A difference in the records of this nature may indicate the seasonal pattern in parameter signals i.e. winter levels against spring levels. At Danby nitrate is consistently within the range 0.5- 0.6 mg l^{-1} which is encouraging in light of the 1.0 mg l^{-1} referred to by Skinner *et al.* (2003). However, at both Lealholm and Grosmont the nitrate concentration is ~1.1- 1.2 mg l^{-1} which does exceed the suggested limit for juvenile pearl mussels. This may therefore link to the fact that four days earlier the stage increased to over 1 m and therefore leaching processes and surface runoff would have been increased. This connects to the assertion that rapid flushing can occur, yet can be followed by lower-level inputs for a 'surprisingly long time' following the initial event (Kirchner *et al.*, 2000: 524). Burt and Arkell (1987) highlight the importance of delayed subsurface flows for nitrate leaching. Therefore, through flow from fields within the catchment would maintain the nitrate concentration at threatening levels. This assertion hints to the question of exposure time; do pearl mussels cope with extended high levels of nitrate in the period following an event?

5.5.2 How does the water quality respond to an increase in discharge?

To understand the influence of higher flows on the water quality, float switches on autosamplers were utilised. Figure 5.8 demonstrates how the stage changed during a period of rainfall in mid-March 2010. The stage records at Danby and Grosmont are similar demonstrating a steep rising limb compared to more gradually decreasing recession limbs. Over a period of 4-hours Grosmont stage rises from ~55 cm to ~90 cm whereas Danby stage rises from ~30 cm to ~70 cm. The flashy regime of the Esk at Danby is confirmed by the nature of this hydrograph; stage reacts slightly more rapidly to precipitation and the recession limb has a steeper descent compared to that at Grosmont. This may be an indicator of greater connectivity in the catchment area adjacent to the Esk at Danby compared to downstream at Grosmont. This may also suggest that the influence of the proximity to the headwater catchments where topography is steeper and water may therefore be transferred more swiftly from rainfall to river water. The more gradually falling recession limb at Grosmont denotes longer travel times and a greater contribution from through flow as opposed to overland flow compared to at Danby. It may also indicate the input from the Murk Esk just upstream of the Grosmont site. The Murk Esk is a significantly sized tributary relative to others in the catchment draining 90 km^2 of land which equates to 25% of the Esk catchment area (EA, 2005); therefore significant inputs from this system contribute to the maintenance of river level and a more gradual recession limb.

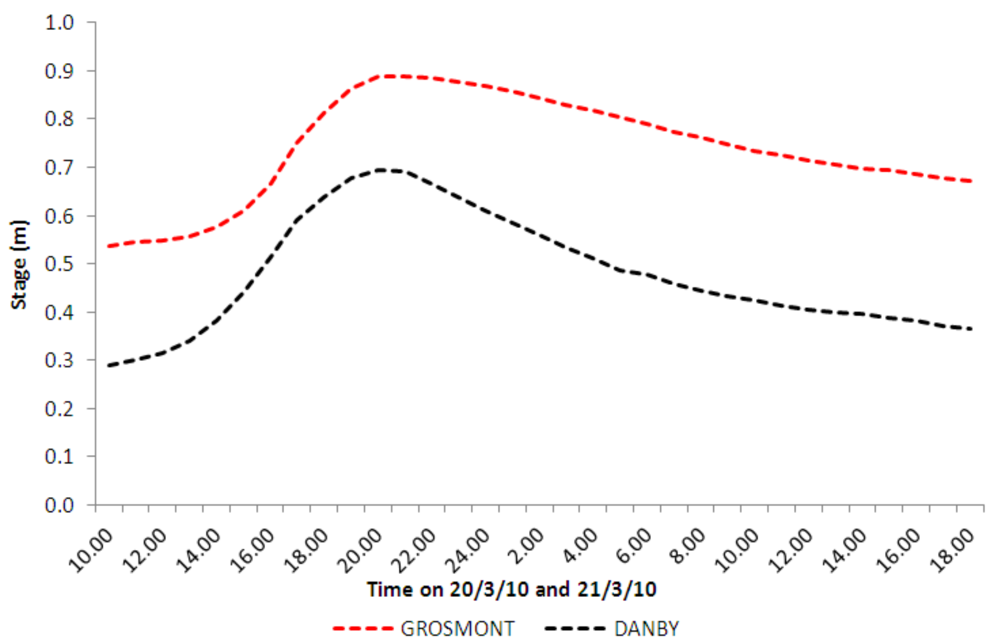
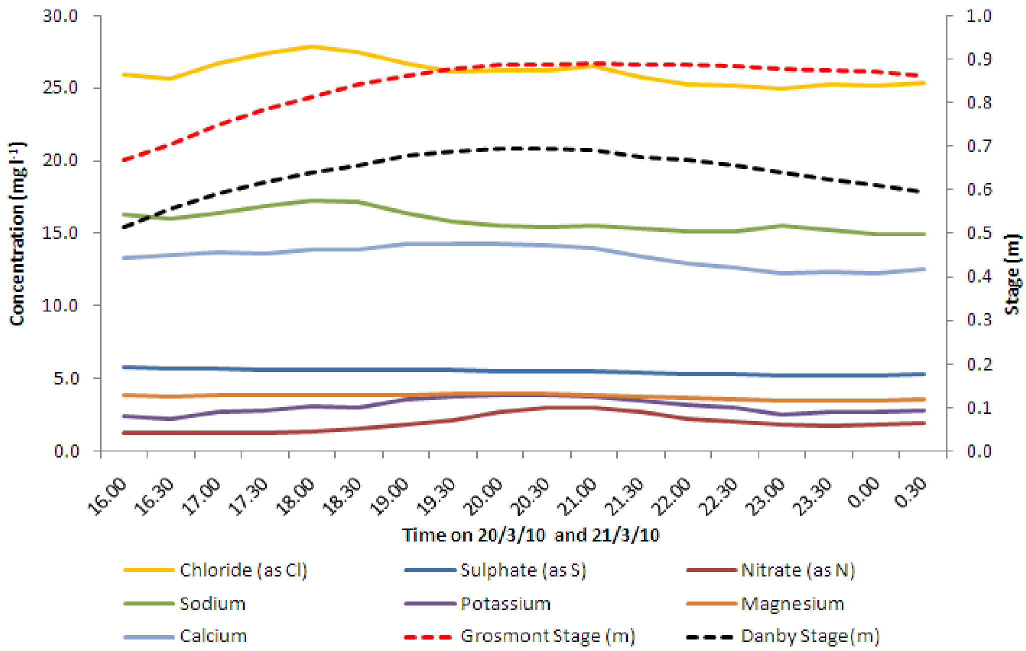


Figure 5.8: An example of flow in the River Esk

The rainfall event triggered autosamplers at Lealholm and Grosmont at 16:00 hrs on 20/3/10 sampling at a 30-minute intervals until 00:30hrs on 21/3/10; this is therefore from early in the period of catchment ‘reaction’ and through the peak stage until the stage returns to base level. Figure 5.9 demonstrates how the concentrations of anions and cations change when the stage is variable.

a. Lealholm



b. Grosmont

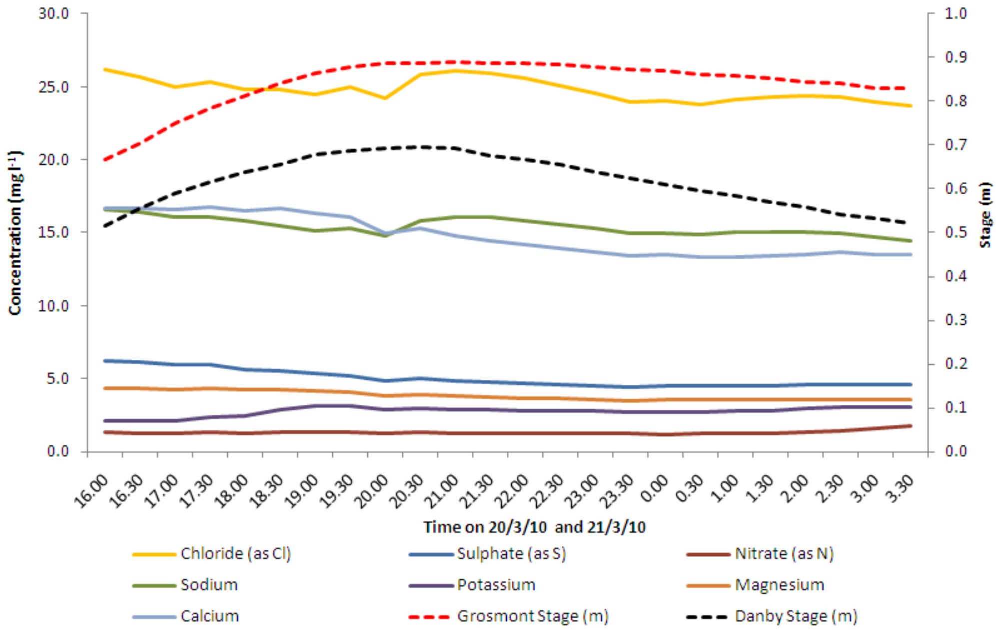
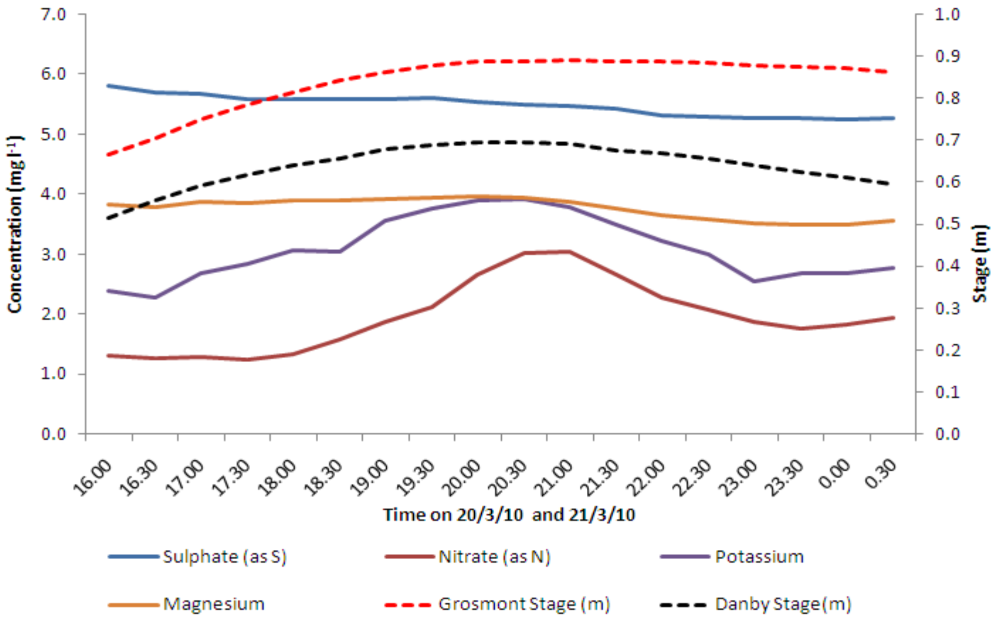


Figure 5.9: Anion and cation concentrations at (a) Lealholm and (b) Grosmont over the rainfall period on 20/3/10 and 21/3/10

Figure 5.9 reveals similar trends between the two sites at Lealholm and Grosmont. At Lealholm and Grosmont Figure 5.9 indicates an element of dilution of components such as chloride, sodium, calcium, sulphate and magnesium which is the typical response of solutes to an increased discharge in a river network (Stott and Burt, 1997). The dilution is not major, for example in the case of sodium at Lealholm concentrations fall from ~17-18 mg l^{-1} to 15 mg l^{-1}. Secondly at Lealholm it appears that the main period of concentration decline for many of these parameters occurs in conjunction with the end of the rising limb of the hydrograph at Danby and Grosmont. It should be noted the solute flux, that is a function of discharge and concentration, and in this the modified conditions dilute sources (lower solute flux) and more concentrated sources (higher solute flux) combine to change the concentration (overall relatively small dilution effect). This dilution occurs as like many other small catchments the Esk responds quickly to rainfall (Kirchner, 2003) and as the baseflow of river water is diluted by new water, the chemical parameters decrease in concentration (Walling and Foster, 1975). Calcium at both sites seems to react to the input of discharge at a delayed interval compared to other parameters such as sodium, chloride and sulphate. The trends presented by sodium and chloride are roughly identical in form as expected due to their ionic affinity to one another. At Lealholm (Figure 5.9a) an increase of ~1-2 mg l^{-1} in the nitrate and potassium concentrations is visible directly after the peak in the stage records. Potassium seems to react more immediately to the stage increase than nitrate which is unusual considering it is less mobile than nitrate (Stott and Burt, 1997). However, potassium can be associated with suspended sediments that will quickly be removed into the channel by surface runoff in the initial high energy phase at the start of the event when most available sediment is transferred (Walling and Foster, 1975). Three mechanisms by which potassium can be sourced are from the leaching for fertilisers, the weathering and erosion of resident geologies and via the plants as they reach the end of the growing season or die. Nitrate can be sourced from livestock and animal wastes, inorganic fertilisers, and vegetation (including debris) (Heathwaite *et al.*, 1993; Hem, 1985).

To gain a clearer representation of some of the trends identified above Figure 5.10 examines some of the lower concentrated parameters. To achieve this higher resolution the scale has been modified:

a. Lealholm



b. Grosmont

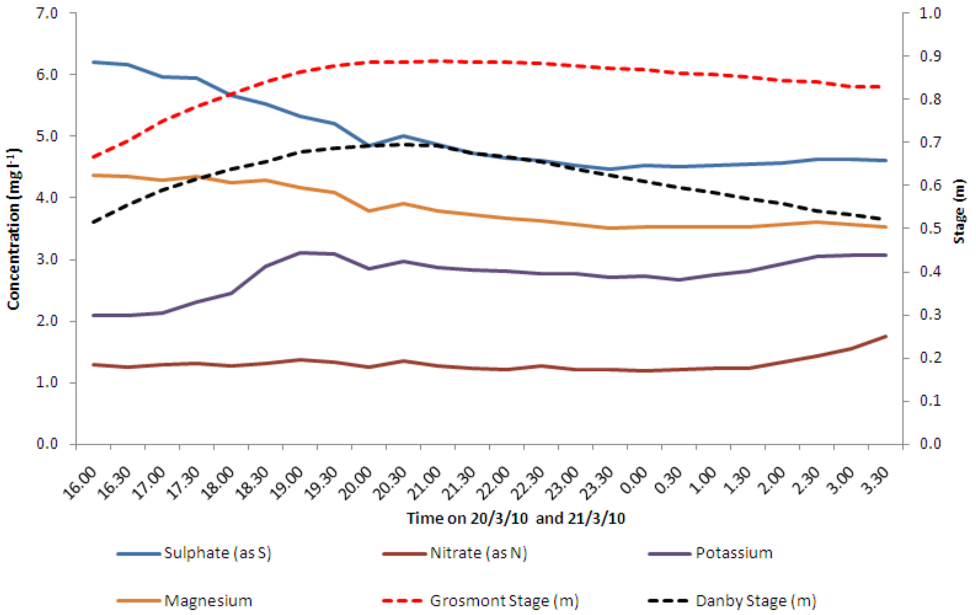


Figure 5.10: Sulphate, nitrate, potassium and magnesium concentrations at (a) Lealholm and (b) Grosmont over the rainfall period on 20/3/10 and 21/3/10

Concentrations in Figure 5.10 confirm the trends highlighted above; the dilution of sulphate and magnesium is greater in the first few hours of the data record as at this time the stage is rising and so rainfall/overland flow/through flow was greater after 19:30 hrs/ 20:00 hrs. The patterns exhibited by both sulphate and magnesium are very similar, signifying an apparent link between the parameters; this evidence combined with the fact that the Dionex measures individual components and not compounds means it is very likely to indicate that the signal of magnesium and sulphate relate to the magnesium sulphate compound. There is a simultaneous dip in concentrations of sulphate and magnesium, as well as potassium; this could be evidence for high-intensity rainfall inputs and rapid overland flow (reducing time for leaching from soils). Potassium and nitrate, both typically increase in response to discharge (Walling and Foster, 1975) and are significant indicators of pollution; they are therefore indicative of the water quality and are analysed in greater depth below.

5.5.3 How does the potassium concentration respond to an increase in discharge?

Potassium is a vital element to flora and fauna, a fundamental element necessary for the growth of vegetation (Hem, 1985); this function has led to potassium being a major component of fertilisers (Stott and Burt, 1997). Potassium is lost from soils by both leaching and surface runoff; it is thus worthwhile analysing the response of a higher discharge on potassium concentration in the Esk to see if these signals are present. Figure 5.11 represents the response of potassium concentrations at Lealholm and Grosmont to the stage fluctuations discussed in depth above.

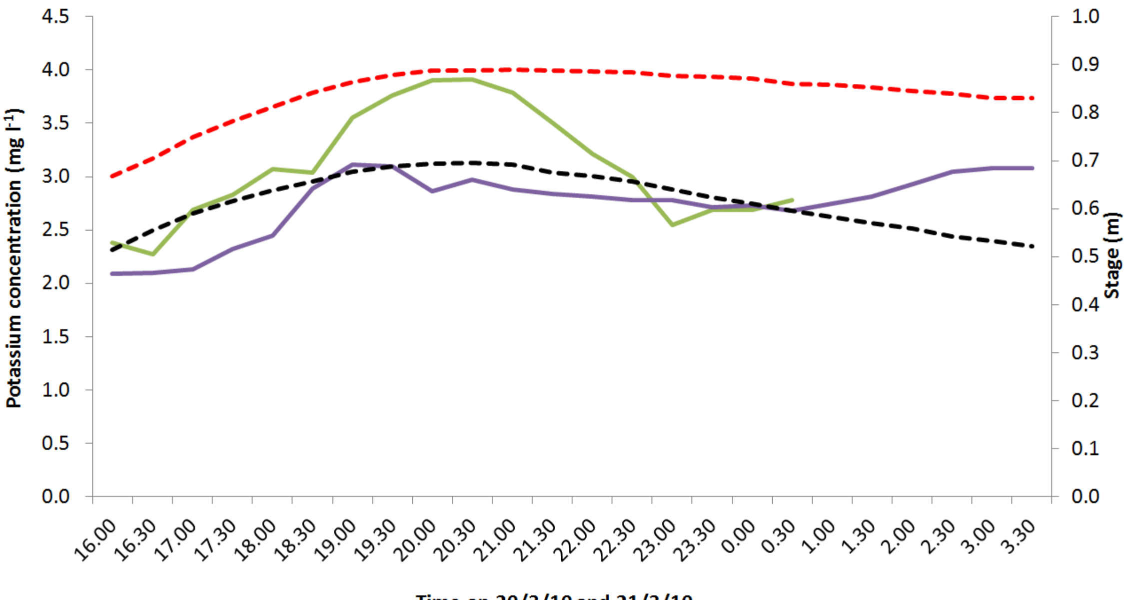


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Figure 5.11: Potassium concentrations at the Esk at Lealholm and Grosmont with the Esk at Danby and Grosmont stage records

There is an observable increase in potassium concentrations at both Grosmont and Lealholm for the duration of the rising limb of the stage hydrograph, which therefore demonstrates the typical concentration pattern response during the period of a storm hydrograph; an increase in concentrations (Walling and Foster, 1975). The typical mechanisms influencing potassium loss from the catchment/additions of potassium to the watercourse are ‘the interaction of hydrological pathways with organic and inorganic sources of potassium, sediment inputs and the chemical properties of the transporting water' (Stott and Burt, 1997:190). Catchments and sub-catchments vary significantly and therefore the specific make-up and mechanism of these processes is complex to predict. This increase in potassium levels could also relate to surface runoff mobilising potassium available in decomposing plants (Hem, 1985; Giusti and Neal, 1993). At Lealholm the peak is more defined and concentrations extend over a larger range; from a minimum of 2.3 mg l^{-1} at 16:30 hrs to a maximum of 3.9 mg l^{-1} at 20:00 hrs giving a range of 1.6 mg l^{-1}. At Grosmont concentrations increase from a minimum of 2.1 mg l^{-1} to a maximum of 3.1 mg l^{-1}, a range of 1 mg l^{-1}. This may be an indication that the catchment is flashier in response to rainfall further upstream. Therefore, with inputs arriving in the network channels at a greater rate, leached potassium also arrives in the river network. This concept of water delivery time period adds weight to argument that at Danby the catchment responds faster to precipitation than at Grosmont. The concentration at Lealholm rapidly decreases from its maximum level to concentrations similar to Grosmont, whereas the concentrations at Grosmont reduce gradually remaining just below the maximum figures recorded. Both signals demonstrate evidence of an increase in concentration towards the end of the sample period; this could be as a result of sub-surface inputs to the river network that have leached potassium from soils. Grosmont provides stronger evidence to this end as the sampler's battery life enabled an extra 6 samples to be taken at this site. To place Figure 5.11 in context, Figure 5.12 illustrates the catchment average concentrations of potassium and the levels found at Lealholm and Grosmont over the 8-month sampling period:

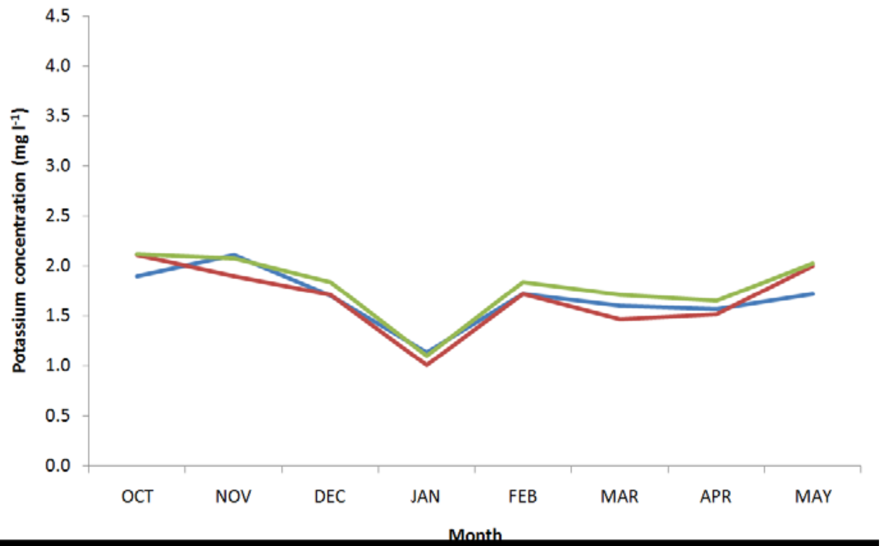

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Figure 5.12: Monthly potassium concentrations at Lealholm; Grosmont; and catchment scale (monthly average)

Figure 5.12 shows how the monthly records from Lealholm and Grosmont are similar with concentrations varying from ~2 mg l^{-1} at the end of 2009 that gradually decline to a minimum in January nearer to 1 mg l^{-1}, followed by a rise to figures falling in the range of 1.5-2.0 mg l^{-1}. The catchment monthly average (average of all 20 sites monitored each month) also reflects this pattern. The minimum concentration reported in Figure 5.11 is 2.1 mg l^{-1} which is higher than the majority of all values reported in Figure 5.12. Many monthly runs were conducted whilst the system was in a steady state (equilibrium) and therefore not receiving large quantities of ‘new’ water from surface runoff/sub-surface flow (Kirchner, 2003); thus it is interesting to note and in agreement with Giusti and Neal (1993) that the solute concentration of potassium increases based on discharge. The March monthly run (conducted on 22/3/10; approximately 30-hours after the event) recorded a catchment average of 1.6 mg l^{-1} indicating that in the following 30-hour period, before catchment sampling began on the 22nd March, the flushing/leaching of soils and resulting mobilisation of potassium and overland flow/through-flow had returned to typical background levels for springtime.

5.5.4 How does the nitrate concentration respond to an increase in discharge?

Nitrate has been identified as a key pollutant within catchments (Heathwaite *et al.*, 1993) and is of particular significance to the freshwater pearl mussel (e.g. Skinner *et al.*, 2003); therefore, it is important to assess how concentrations of this anion is influenced by river discharge/rainfall inputs in a catchment. As nitrate is more mobile than potassium (Stott and Burt, 1997), it would be expected that losses would be higher and as significant, compared to those presented above for potassium concentration, over the 12-hour period on 20/3/10 and 21/3/10. It should be acknowledged that variable source areas within catchments can mediate the level of nitrate inputs (Poor and McDonnell, 2007; Johnes and Burt, 1993); thus catchment characteristics influence the response to discharge. Figure 5.13 demonstrates the nitrate concentrations during the event at Grosmont and Lealholm.

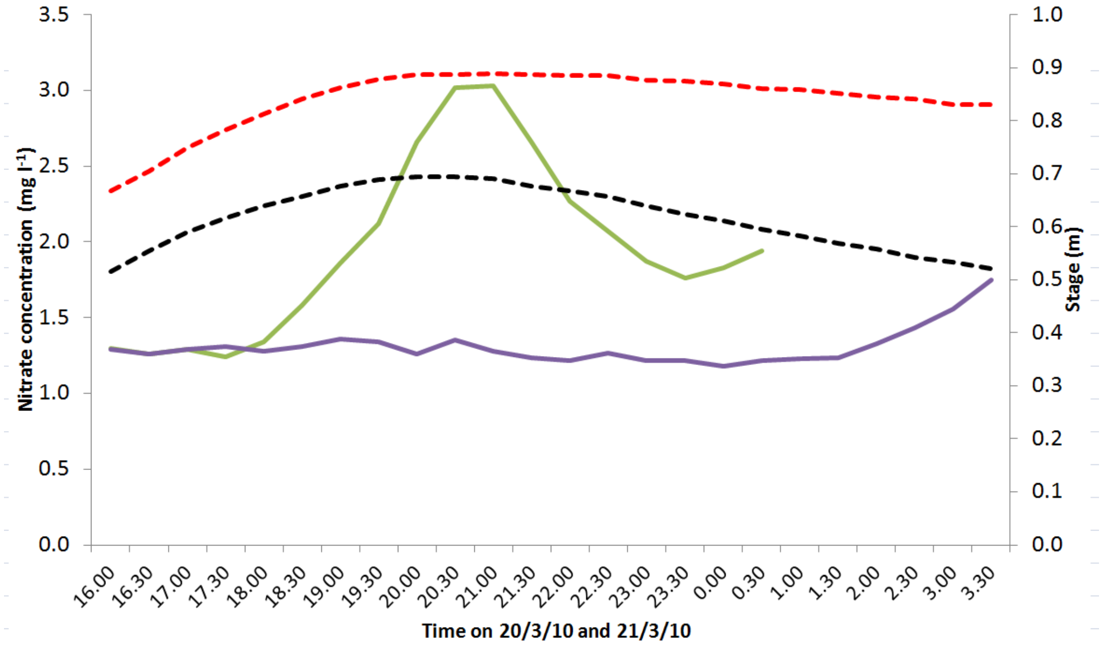

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Figure 5.13: Nitrate concentrations at the Esk at Lealholm and Grosmont with the Esk at Danby and Grosmont stage records

There is a notable difference between the signal at Lealholm and Grosmont; this could relate to the difference in source areas between the two sites as discussed in the literature (e.g. Johnes and Burt, 1993). Firstly, the Lealholm concentrations increase from 1.2 mg l^{-1} at 17:30 hrs to peak at 3.0 mg l^{-1} at 20:30 hrs. The trend is steeper and more pronounced than the stage records for both Danby and Grosmont. The peak in nitrate at Lealholm occurs at the same time as the peak in the stage records at ~20:00 hrs. This evidence agrees with the scientific understanding that typically during storm periods nitrate levels fluctuate due to runoff created from a larger and different range of source areas and via a number of generation mechanisms (Johnes and Burt, 1993). Similar to the potassium concentration at Lealholm, the nitrate concentration decreases from its maximum rapidly compared to the slowly declining stage record, yet remains elevated just under 2 mg l^{-1} suggesting that sub-surface input and delayed surface runoff maintains the concentration. This immediate decrease concurs with the theory that 'a rapid decrease in nitrate concentration is characteristic of flood events during winter and spring' (Johnes and Burt, 1993:294).

The nitrate concentration at Grosmont does not follow the same trend as at Lealholm (unlike the analogous potassium patterns); it fluctuates between 1.1 mg l^{-1} and 1.3 mg l^{-1} before demonstrating an increase at 02:00 hrs (21/3/10) to a maximum of 1.75 mg l^{-1} where records finish. Webb and Walling (1983) propose that even in small catchments signals can vary according to factors of antecedent conditions and rainfall intensity. The Lealholm signal reveals an increase in concentrations in the last hour of its samples. Therefore it can be hypothesised that concentrations would continue to increase before the river returned to base level and the concentrations equilibrated and returned to consistent values (as discussed in section 5.5.1). This hypothesis of increasing nitrate concentrations in the following hours, during the recession period of the stage records, would indicate the typical pattern of peak concentration lagging behind the peak in stage/discharge expected from nitrate/stage (discharge) relationships (Johnes and Burt, 1983).

Crucially, all samples analysed here (42 samples; 24 at Grosmont and 18 at Lealholm) are over the 1 mg l^{-1} tolerance level for freshwater pearl mussels as postulated by Skinner *et al.* (2003) and Bauer (1988). Figure 5.15 illustrates the typical nitrate concentrations discovered at Lealholm and Grosmont when the stage is not fluctuating as with this event.

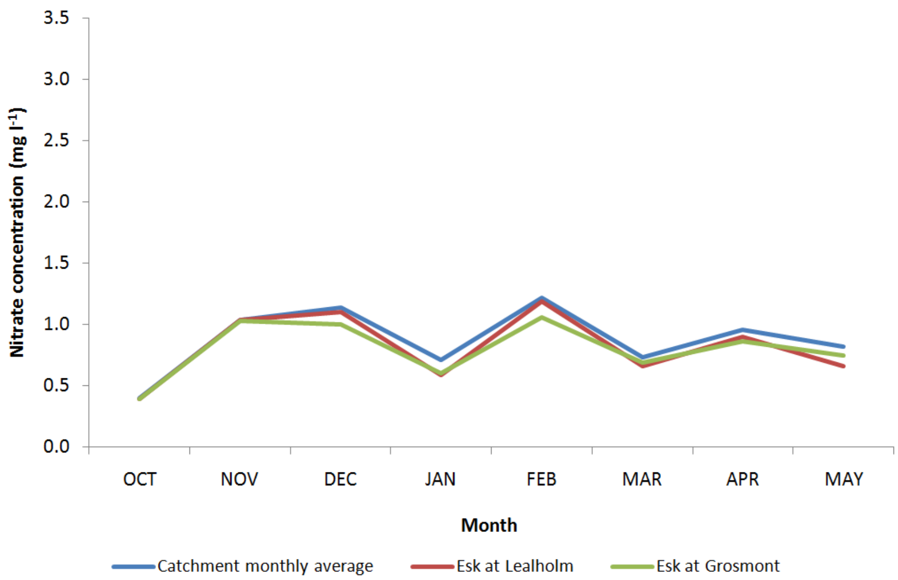

Figure 5.14: Monthly nitrate concentrations at Lealholm; Grosmont; and catchment scale (monthly average)

Figure 5.14 demonstrates that typically the Esk catchment monthly averages of nitrate concentration varying from 0.4 mg l^{-1} to 1.2 mg l^{-1}. Both Grosmont and Lealholm exhibit the same trend (yet at Grosmont the range of concentrations is smaller). This indicates that even in more steady state of flux at these sites in the Esk the 1 mg l^{-1} tolerance level is under threat and is occasionally overcome. However, the levels displayed in this monthly record indicate that the records generated over the 20/3/10 event are almost certainly generated as a by-product of the rise in stage during flood events. Even though this graph spans an 8-month time frame a seasonal cycle is present, as with many rivers in respect to nitrate concentration (Johnes and Burt, 1993). This is indicated by high nitrate concentrations in the wetter winter months and lower levels spring/summer and even in this case low levels in autumn (October). This pattern bears similarities with the seasonal nitrate trend found in the Dart catchment by Webb and Walling (1985) with maximum concentrations in December and minimum values in late summer and early autumn. This trend is echoes past research findings that, for example, found that 'total nitrate losses are strongly seasonal, with 80% of the load exported in December to February inclusive' (Johnes and Burt, 1993: 291)

5.5.5 How does suspended sediment respond to discharge?

It is also interesting to look at how suspended sediment values change in higher stage as they are often associated with contaminants. A second reason for addressing this parameter at high flows is that sedimentation has been suggested to be a significant reason for the decline in freshwater pearl mussels in the Esk (Environment Agency, personal communication), although more recent research has suggested has suggested water quality problems may play a role (Bracken, 2009). Figure 5.15 represents how suspended sediment concentration changed in response to the event on 20/3/10:

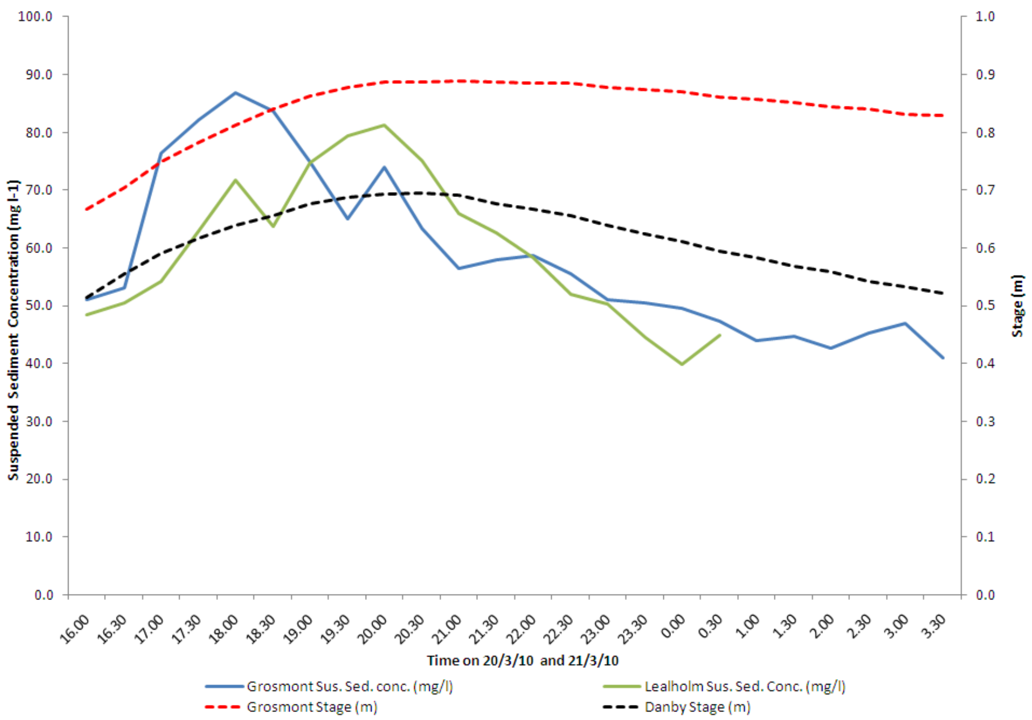

Figure 5.15: Suspended sediment concentrations at the Esk at Lealholm and Grosmont with the Esk at Danby and Grosmont stage records

Similar to nitrate and potassium, suspended sediment concentration (SSC) increases with stage. Both sites demonstrate similar patterns. At Grosmont SSC increases sharply from ~50 mg l^{-1} to peak at ~85 mg l^{-1} at 18:00 hrs, prior to the peak in stage ~2 hrs later. This is followed by a gradually recessional trend to 40 mg l^{-1} where records finish at 03:30 hrs. SSC at Lealholm increases at a lower rate compared to the Grosmont record yet reaches a maximum ~80 mg l^{-1} at 20:00 hrs which is the same time that stage peaks. The following 9 samples at Lealholm indicate a greater rate of decline compared to that of Grosmont. The higher SSC at Grosmont could be related to the fact that a larger amount of water will be in the channel at this location in the catchment and therefore the erosive power of the water will affect a larger area in the channel. Secondly, at Grosmont a greater total contribution of water washed off source areas (including some only utilised in storm events) will influence the record than at Lealhom. At base levels the suspended sediment concentrations have values typically ranging from 5-20 mg l^{-1} (section 5.5.1 gives a greater level of evidence to this end).

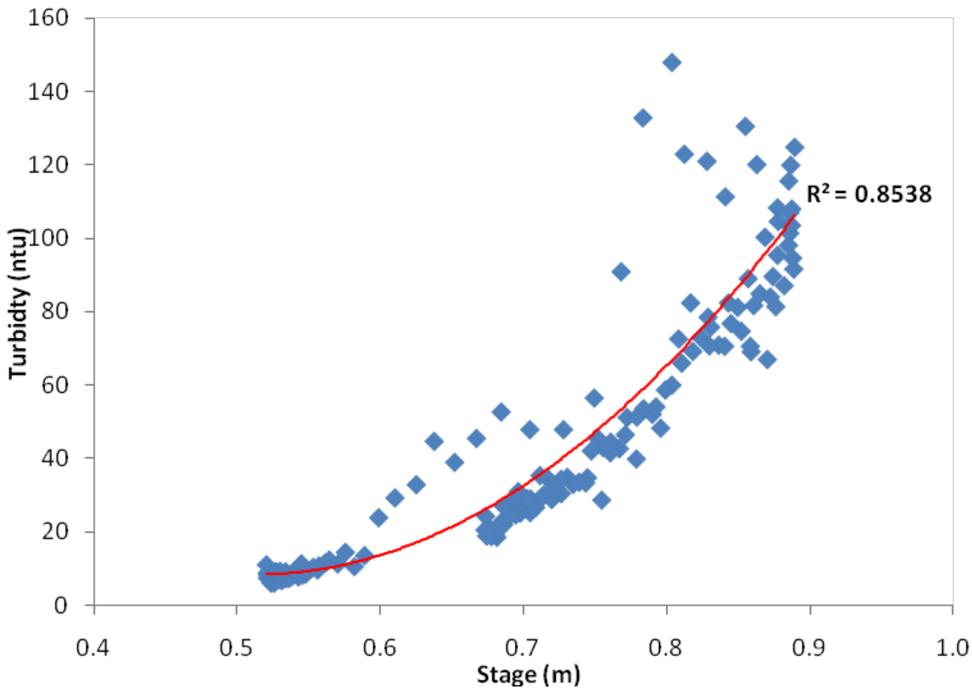

Figure 5.16: The relationship between turbidity and stage at Grosmont

Figure 5.16 demonstrates how SSC increases with stage; it uses the turbidity and stage records from the data logger at Grosmont from 00:00 hrs on 20/3/10 to 18:00 on 21/3/10. Turbidity is a measurement of SSC in the river and so can be effectively used as a proxy. There is a direct relationship (polynomial) between the data with an r^2 value of 0.85. It reveals that, as stage increases, turbidity increases but by a greater magnitude. Another observation is that when the stage is higher, the turbidity is more variable which indicates periodic flushing of sediment into the system during high discharge periods. The scatter present in the record indicates that SSC is not completely caused by changing discharge i.e. there are other factors influence its presence/absence, for example, exposure of banks/uncovered ground.

5.5.6: Hysteresis in water quality variation

When the SSC from the 20/3/10 event at Grosmont and Lealholm are plotted against stage, clockwise hysteresis is exhibited (see Figure 5.17). The relationship between suspended sediment and stage during storm events is not usually homogeneous and they often produce hysteretic loops (Seeger *et al.*, 2004). Clockwise hysteresis indicates higher concentration on the rising hydrograph limb compared to lower concentrations on the recession limb (House and Warwick, 1998). Klein (1984:256) postulates that for SSC 'the common clockwise hysteresis occurs when the sediment contributing area is the channel itself, or the adjacent area' and therefore it is fair to deduce that the evidence below indicates that the sediment derived in this period of the event was localised to the areas nearby to the channel and/or mobile sediments within the channel area too. The clockwise hysteresis displayed in Figure 5.17 is the typical result in smaller catchments and thus the clockwise trend displayed in each diagram is expected. Figure 5.17 uses stage data from the data loggers at Danby and Lealholm; it should be noted that at Lealholm, as no data logger is available, stage data from both sites is used to form a hysteresis curve (Danby stage- red loop; Grosmont stage- blue loop).

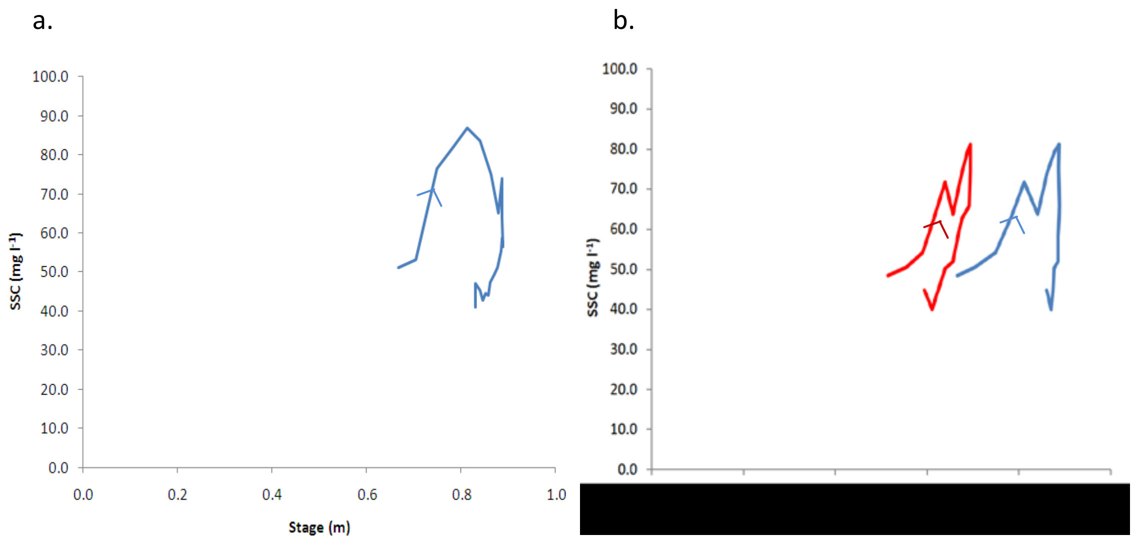

Figure 5.17: Suspended sediment concentration (SSC) storm hysteresis loops at (a) Grosmont and (b) Lealholm, from the 20/3/10 event

Figure 5.18 investigates the relationship between nitrate/potassium and the stage records over the duration of the storm event on 20/3/10. Figure 5.18 (b1 and b2), like Figure 5.17b, provides curves using stage data from both Danby and Grosmont. At Grosmont (a1 and a2) a small amount of clockwise hysteresis is displayed. The trend in a1 indicates that as the stage increases there is no increase in nitrate, yet as stage decreases nitrate starts to increase; this could highlight the influence of sub-surface processes mobilising nitrate and sub-surface water being received in the river system. A similar trend is revealed in a2 with an increase in concentration on the recession limb; however, there is a more immediate increase in the potassium concentration in response to the increase in stage on the rising limb. At Lealholm (b1 and b2) it appears that clockwise hysteresis is the dominant trend with the highest concentrations on the rising limb. However, the Danby stage data with nitrate reveals anticlockwise hysteresis and therefore a pattern with higher nitrate concentration on the recession limb. This complication highlights the problem of a lack of stage data at Lealholm. These results highlight the importance of contribution to the system of nitrate and potassium via sub-surface processes.

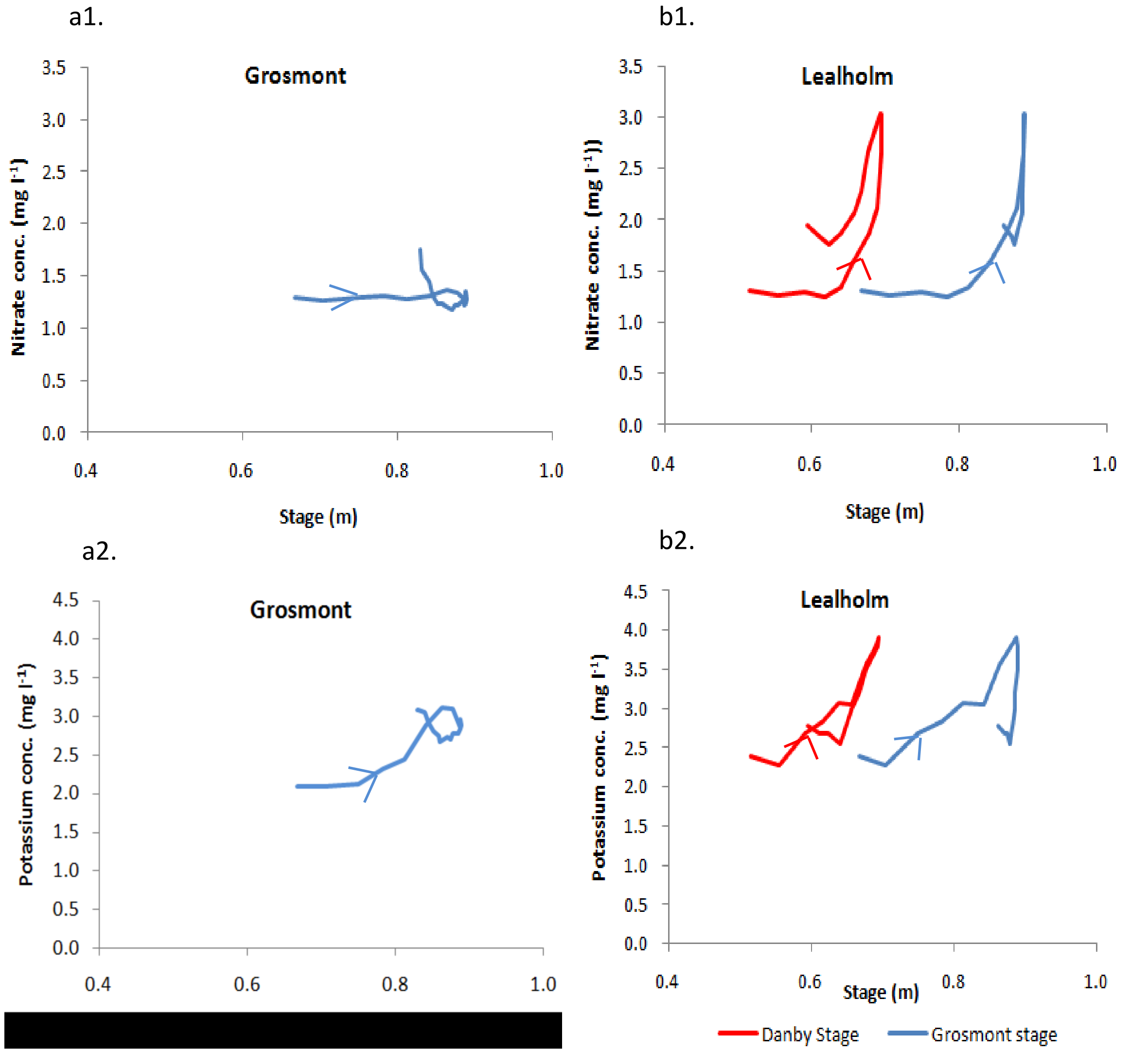

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Figure 5.18 Nitrate and potassium storm hysteresis loops at (a) Grosmont (a1 and a2) and (b) Lealholm (b1 and b2), from the 20/3/10 event

To make the link between SSC and nitrate/potassium, Figure 5.19 (a1/2 and b1/2) is used to illustrate how they interact over the period of the 20/3/10 event. Anticlockwise hysteresis is exhibited; the Lealholm data (b1 and b2) indicate almost a parallel increase and decrease of nitrate/potassium concentrations and SSC with higher nutrient concentrations on the recession limb. At Grosmont (a1 and a2) the increase in nutrient concentrations only occurs after the rise in SSC. These data show that nutrient concentrations are higher on the recession limb; this suggests that the desorbing of nutrients from the initial flushing of sediment in the earlier portion of the event has occurred and desorption maintains the concentration at a higher level on the recession limb of the hydrograph. Alternatively, the concentration may be maintained by larger concentrations contributed to the system later in the event via sub-surface processes.

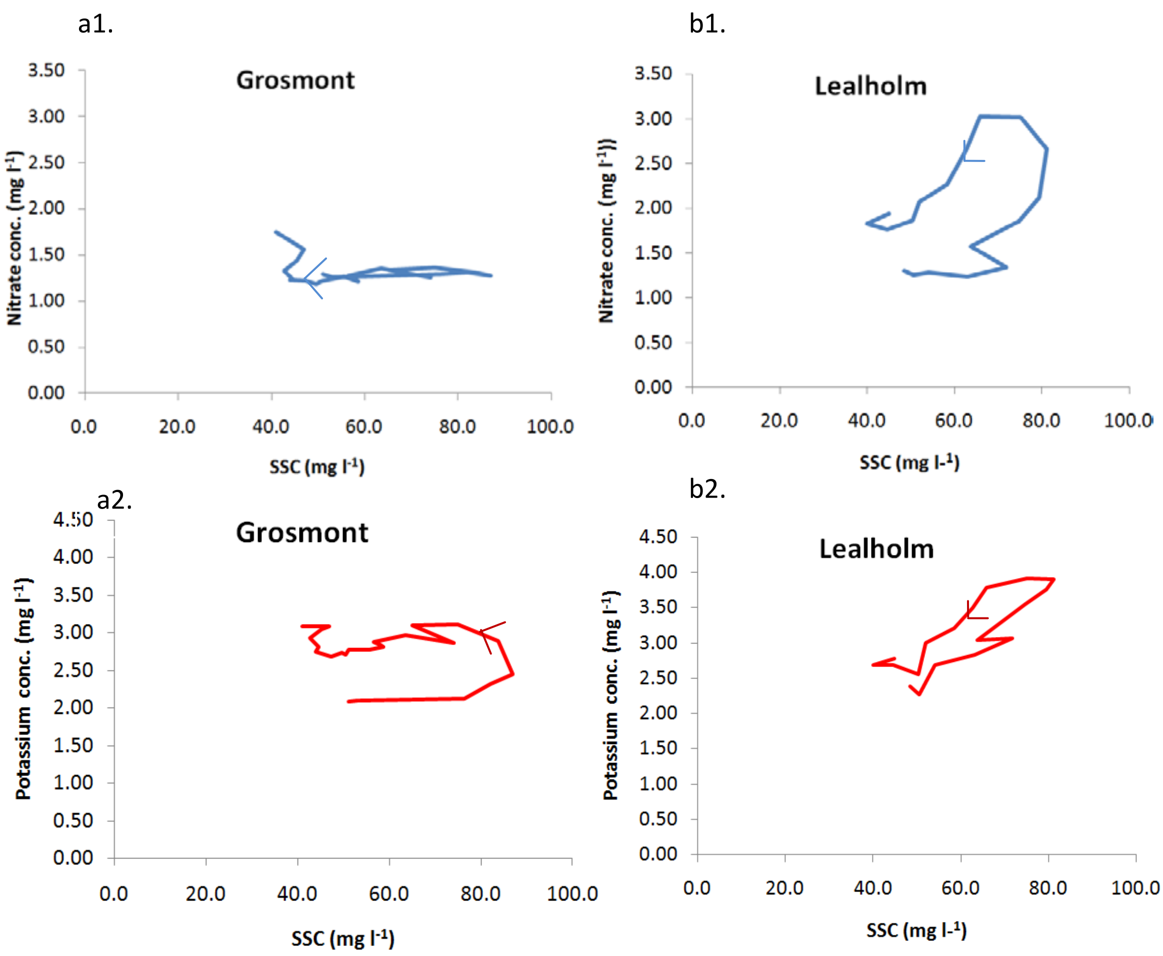


Figure 5.19: Hysteresis loops for SSC at Grosmont and Lealholm against nitrate (blue) and potassium (red) for the 20/3/10 event

5.6 Summary

In summary this chapter has built upon and extended the points illustrated in Chapter 4. It appears that water quality concentrations over the monitoring period do vary within the catchment as well as displaying an element of seasonality. The patterns seen in catchment area and land cover sections (5.3 and 5.4 respectively) solidified the assertions made in Chapter 4 and showed these two factors have an impact on concentration dynamics. Section 5.5 illustrated the influence that changing stage can have over the course of short term changes on water quality parameters.

6.0 Accounting for connectivity using SCIMAP

6.1 Introduction

Chapters 4 and 5 presented evidence that land cover exerts a strong influence on in-stream water quality; however, as discussed above a key question is the extent to which land cover is directly connected to the water chemistry. SCIMAP helps to address the connectivity issue and has been applied to the catchment, as described in Chapter 3. SCIMAP uses a measure of connectivity to establish which land covers appear to be responsible for diffuse pollution. SCIMAP is a risk-based model that identifies high and low risk land covers by combining: the spatial distribution of land cover, a simple hydrological connectivity index (the network index; Lane et al., 2004) and in-stream nutrient measurements. It works on the principle that contaminants within the catchment are transferred via hydrological flow paths to reach a river network (Lane *et al*., 2006). The pollution is either detected by monitoring (used in this work, see Chapter 3) or by notable water quality problems (e.g. excessive algal blooms, fish kills; Lane *et al.* 2006). When the source of diffuse pollution can be identified, land management can be focussed on the areas that most strongly influence the water quality of the system. SCIMAP allows us to: firstly, identify the land covers that appear to be responsible for in-stream nutrient concentrations accounting for their connectivity; and secondly, extend our analysis to the whole catchment as opposed to the 20 sites analysed in chapters 4 and 5. However, it must be acknowledged that SCIMAP assumes that: 1) topography exerts the primary control on the spatial pattern of wetness in agricultural catchments, which may not always be the case (Lane *et al.*, 2006); and 2) certain land covers are more likely to produce risks than others.

6.2 Results

The model output has been used to create dotty plots and uncertainty plots for all of the parameters in the study. Following Beven and Binley (1992) dotty plots are scatter plots of a model parameter on the x axis against model performance on the y axis. In this case they show the relationship between the land cover risk weighting (on the x axis) and the model performance quantified by the correlation coefficient (on the y axis). Trends in these dotty plots show the importance of that land cover, while the form of the trend indicates the risk weighting that should be assigned to that land cover. For example, for a particular land cover (e.g. improved pasture), a low land cover weighting resulted in a poor model performance (low correlation between predicted risk and observed water quality) whereas a high land cover risk weighting resulted in improved model performance. This provides an indication that: improved pasture is an important land cover (trend in the dotty plot) and that it is a source of diffuse pollution in the catchment. The runs with positive correlations are plotted which can result in varying density of points on the plots. Uncertainty plots assess simulations in light of their correlation coefficient; the standard deviation and mean of the land cover risk weightings is progressively calculated for all simulations above a given correlation coefficient from best runs only (right) to all runs (left). If the range of standard deviation values is small and a land cover has a low risk weighting then the land cover is of low risk. An increase in the mean indicates a heightened pollution risk whereas a decrease shows a reduced pollution/low pollution risk. Standard deviation bands that are narrow indicate the importance of land cover whereas wide bands show that it is less important. The dotty plots and uncertainty plots for nitrate and potassium, nutrients that formed a central part of the analysis, are discussed here (both with and without stream power).

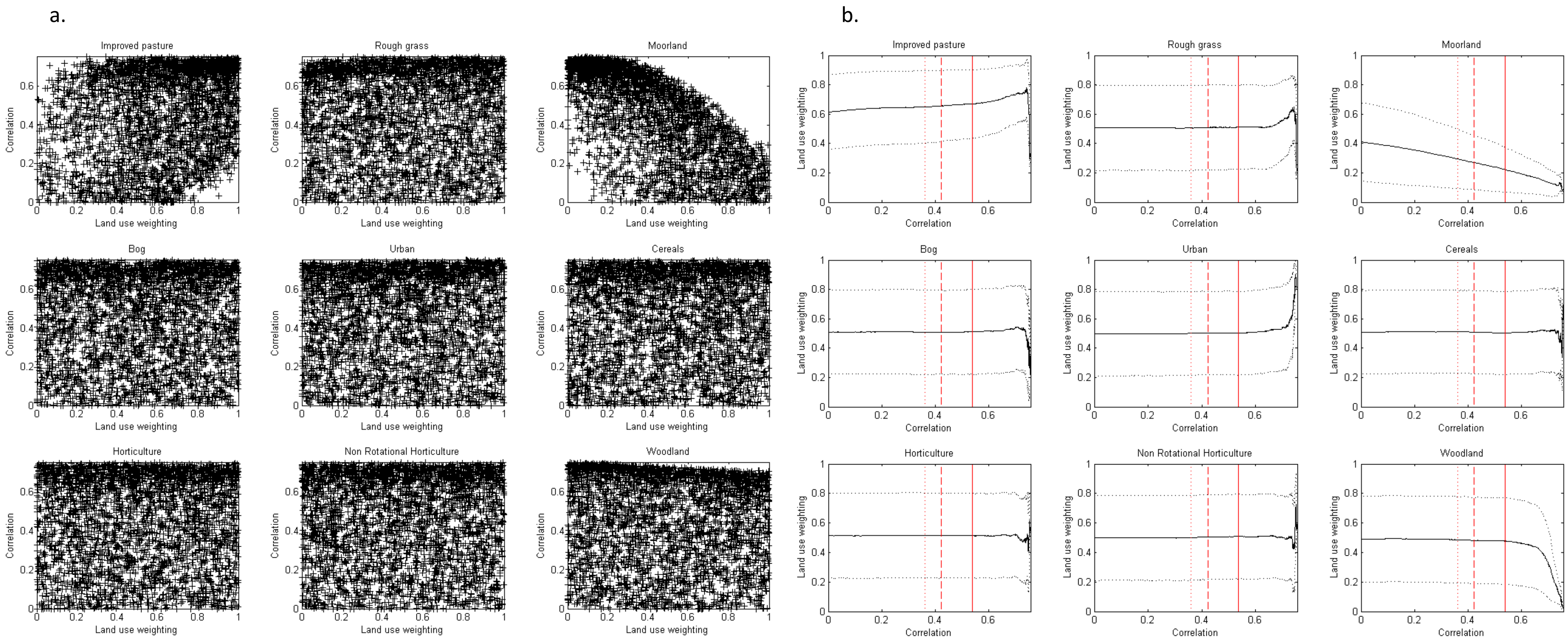


Figure 6.1: (a) Dotty plots of correlation against land use weighting for nitrate (no stream power) and (b) Uncertainty plots of land use weighting against correlation for nitrate (no stream power)

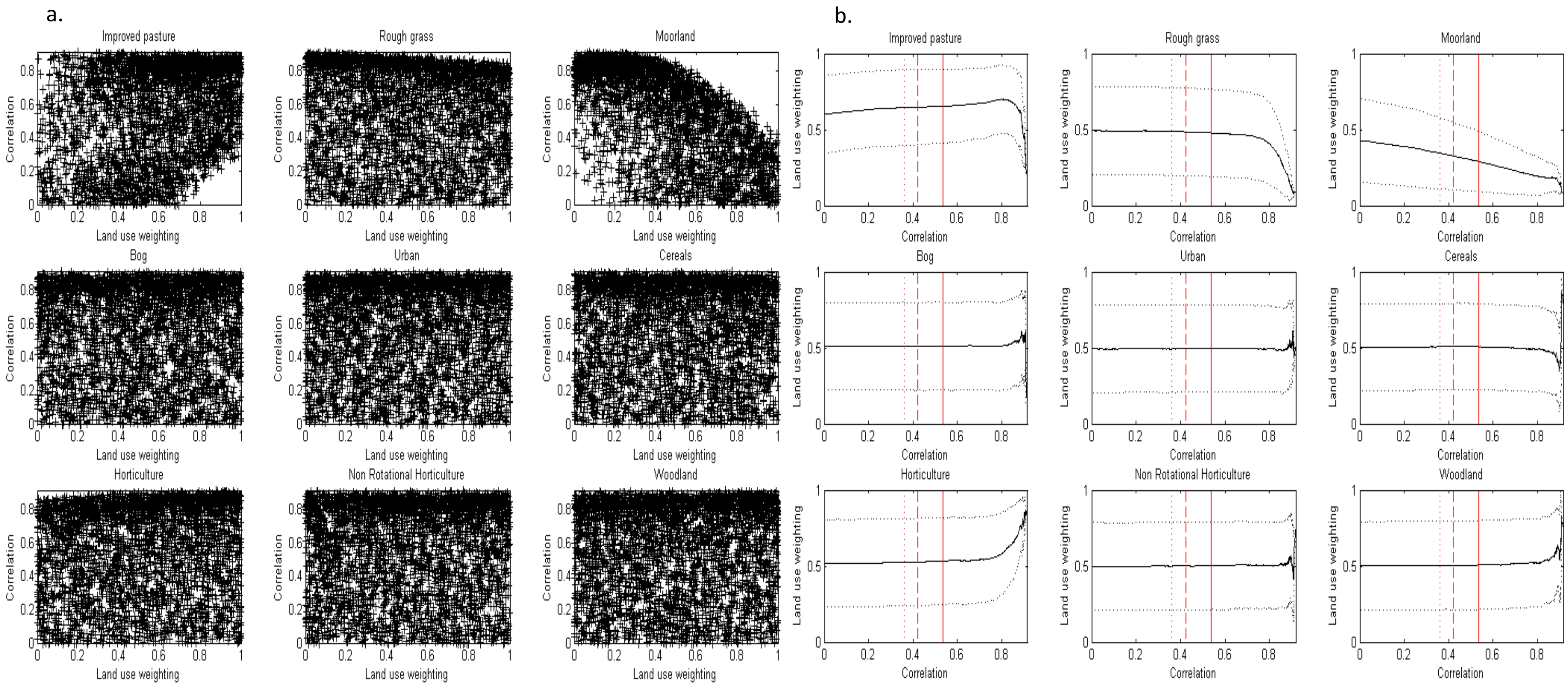


Figure 6.2: (a) Dotty plots of correlation against land use weighting for potassium (no stream power) and (b) Uncertainty plots of land use weighting against correlation for potassium (no stream power)

In Figure 6.1a, investigating nitrate pollution risk, two land cover categories display strong trends: moorland and improved pasture. The woodland and rough grass plots indicate they are low risk and high risk land cover categories respectively, however the relationships presented are weak. All other land covers (e.g. horticulture) demonstrate that the land cover weighting has no control on the resulting correlations which are spread uniformly in the plot; therefore these land covers do not bear a significant influence on the nitrate pollution risk. Nevertheless, as previously indicated, moorland and improved pasture display stronger trends thus allowing for the interpretation of nitrate pollution risk for these particular land covers.

In the moorland land cover plot it can be noted that when the land cover risk weighting is set between 0-0.4, the best model fits (correlations ~0.75) are achieved. This indicates that moorland is an important land cover in the case of nitrate. There is a strong relationship irrespective of other land cover weightings. Therefore, moorland is low risk for nitrate pollution and has controlling influence on predictions. On the other hand, improved pasture land cover has a strong influence upon the nitrate pollution risk. When the land cover weighting is set between 0.8-1 the best model performance is achieved and therefore it can be assumed that improved pasture has a significant effect and that it is high risk.

In Figure 6.1b the majority of plots demonstrate a consistent mean value with broad standard deviation lines; this indicates that the water quality is not affected irrespective of the weighting given to the land cover in question (e.g. cereals). The improved pasture uncertainty plot in Figure 6.1b demonstrates a gradual increase in land cover weighting as the correlation coefficient increases. This indicates pollution risk in areas of the catchment where improved pasture exists. The standard deviation bars narrow, indicating that the importance of this land cover is high. Similarly, the moorland mean values decrease as the correlation coefficient increases and the standard deviation bars narrow; this indicates that moorland is of low risk to the local water quality.

Figure 6.2a and b illustrate a similar picture to that presented in Figure 6.1. Rough grass and horticulture display weak relationships and can be associated with low and high risk respectively. Improved pasture and moorland strengthen the trend of high risk and low risk environments respectively for the in-stream water quality. Both Figure 6.1 and 6.2 address the application of SCIMAP in an environment with no stream power. It is important to consider this aspect as nitrate and potassium can be mobilised in standing surface waters. However we can run SCIMAP to test for the influence of stream power upon the pollution risk in the various land cover categories.

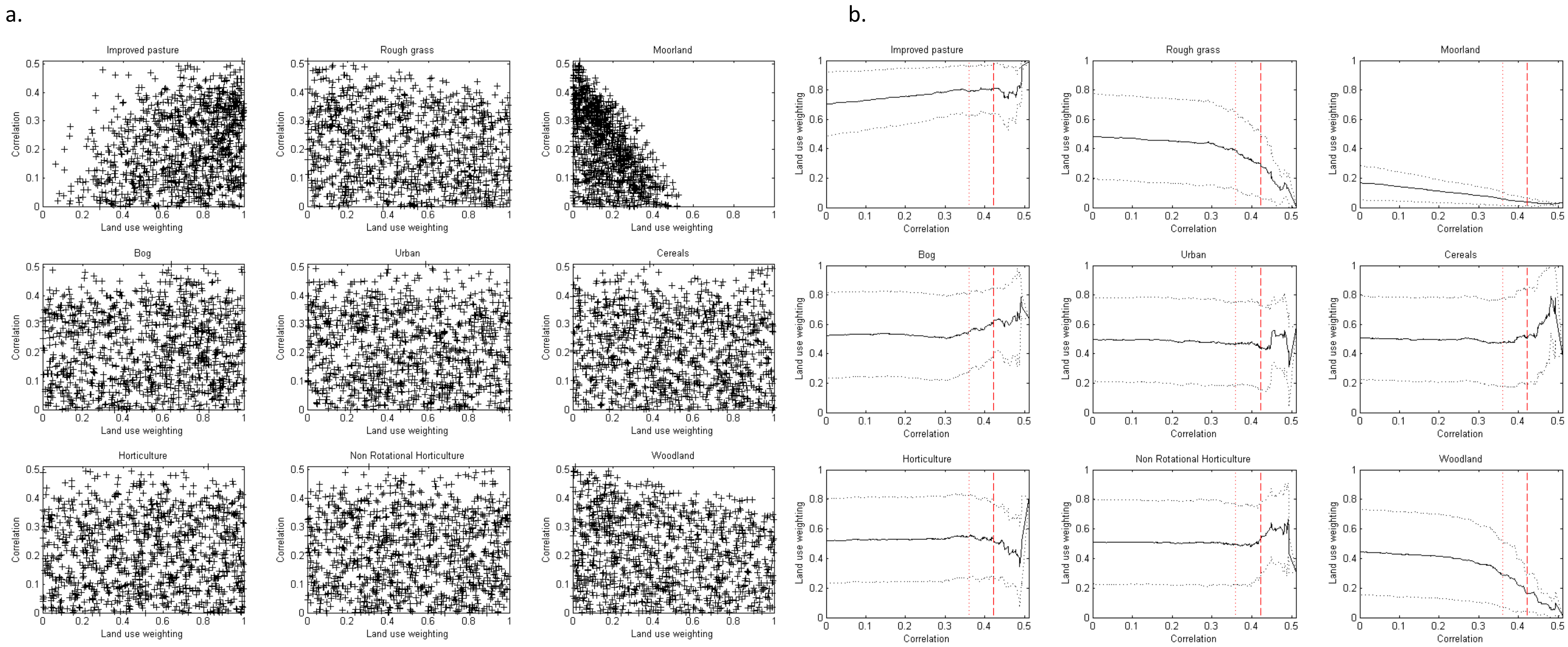


Figure 6.3: (a) Dotty plots of correlation against land use weighting for nitrate (with stream power) and (b) Uncertainty plots of land use weighting against correlation for nitrate (with stream power)

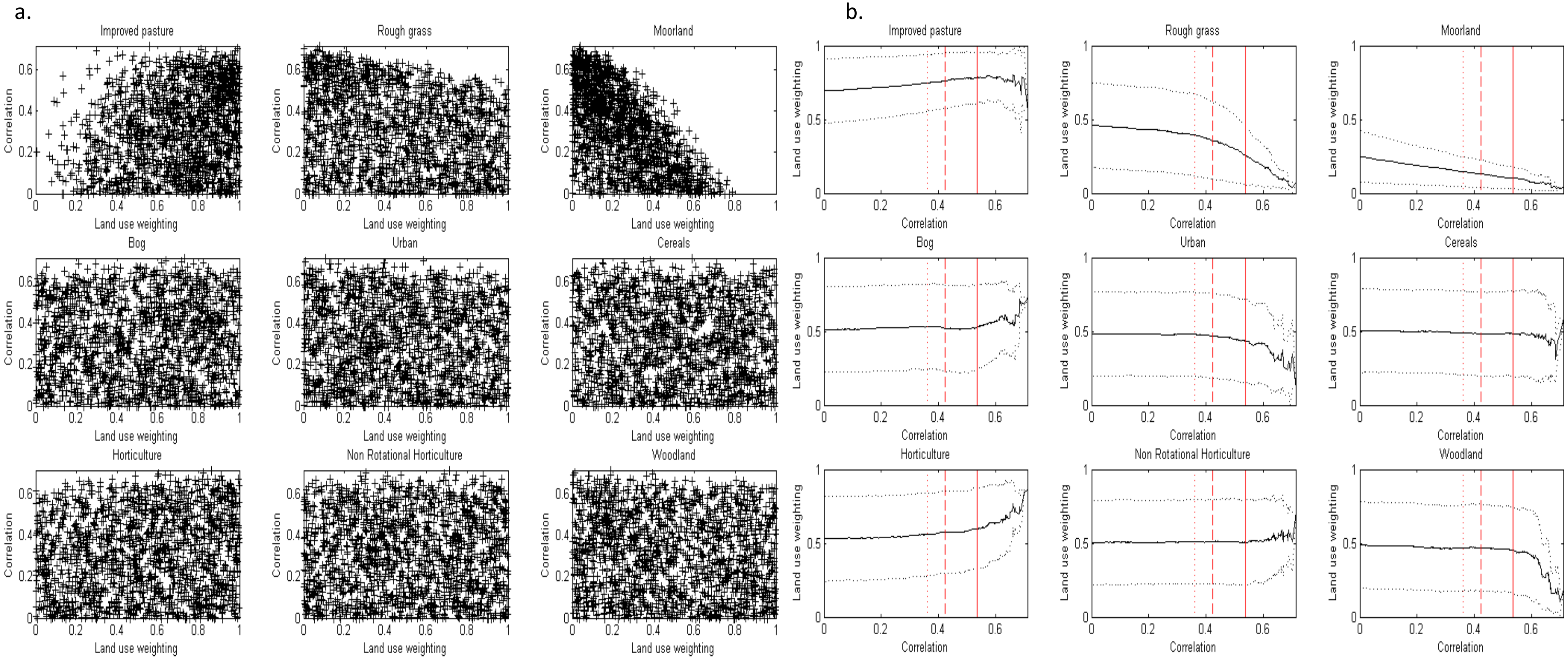


Figure 6.4: (a) Dotty plots of correlation against land use weighting for potassium (with stream power) and (b) Uncertainty plots of land use weighting against correlation for potassium (with stream power)

It is important to both include and exclude stream power as this allows the different forms of nutrient mobilisation to be accounted for (erosion of nutrients bound to soil particles or their dissolution in standing water). By comparing Figures 6.1 and Figure 6.2 with Figures 6.3 and 6.4, we can look at the effect of stream power in SCIMAP. In the runs with no stream power (Figures 6.1 and 6.2) a larger proportion of the 5,000 simulations returned a positive correlation compared to runs with stream power (Figure 6.3 and 6.4), this can be noted by the difference in the density of points when comparing plots. The difference in point density indicates that no stream power produces results closer to the observed values with greater frequency. The clearer trends in Figures 6.3 and 6.4 show that including stream power makes the model more responsive to land cover weightings. This suggests that the land cover weightings assigned from the run without stream power are adjusting to include some mobilisation effects. This would result in increased scatter in the dotty plots which is removed to some extent with stream power. However, higher correlations or better model performance is observed in Figures 6.1 and 6.2 compared to Figures 6.3 and 6.4 suggesting that stream power does not improve model performance. To choose between stream power and no stream power we must consider: 1) stream power version of SCIMAP produces clearer dotty plots and land cover weightings are less scattered so stream power is capturing something, but 2) it is known that nitrate and potassium can mobilise in standing water so stream power is not always necessary, and, 3) there is better model performance with the simpler no stream power model. Therefore the no stream power model will be applied when creating catchment risk maps below.

In Figure 6.3a improved pasture land cover is shown to be of higher risk and a driver of in-stream nitrate when the land cover is given a high weighting. No other land covers revealed this trend. Woodland and rough grass show a weak trend of higher correlations occurring when the land cover is given lower weightings. Moorland displays this trend more than any other land cover type; it has to be weighted between 0 and 0.5 to return a correlation of 0 to 0.5 with monitored in-stream nitrate. This indicates that woodland, rough grass and, especially, moorland are of low risk in terms of nitrate pollution to the river network. The uncertainty plots (Figure 6.3b) confirm the assertion(s) of high and low risk nitrate land cover types; with narrower standard deviation bands for improved pasture and moorland, and wider bands elsewhere.

Figure 6.4 reveals a similar trend for potassium. Most land covers in Figure 6.4a display uniformly scattered plots e.g. bog. Improved pasture is shown to be the land cover of highest risk, giving higher correlations when the higher land cover weightings are applied. Moorland presents low correlations with high land cover weightings and the highest correlations (~0.7) with the lowest land cover weightings (0-0.2). This signifies that moorland is of low risk and that it is likely to be an insignificant driver of in-stream potassium concentration. Figure 6.4b shows a number of increasing trends; notably improved pasture stands out but bog and horticulture display a rise in correlation at the highest land cover weightings indicating these are the high-risk environments. Similarly, decreasing trends reveal the low risk land covers here seem to be moorland, rough grass, woodland and urban. There are more positive correlations in Figure 6.4 compared to Figure 6.3 indicating that stream power is of greater importance when mobilising potassium.

SCIMAP has been a helpful tool to build on the empirical evidence which illustrated the presence of a number of hot spots. To be able to account for connectivity, a major assumption in this work, it is useful to a) confirm the importance of land cover as a driver in the system; and b) assess the relative pollution risk of different land cover types. SCIMAP has strengthened the assertion put forward by the empirical data that suggests improved pasture to be a high pollution risk as seen from good model performance when this land cover type is weighted as a high risk pollution area. It also corroborates the observation that moorland presence leads to lower pollution risk to the in-stream water quality. This agrees with observations made earlier in chapters 4 and 5; for example, at Hob Hole, a catchment with low annual and low monthly nitrate concentrations, there is low pollution risk because there is a high percentage of moorland within the upstream contributing area. Likewise, Toad Beck, which has the highest annual and monthly nitrate concentrations, there is a high pollution risk because there are higher percentages of improved pasture compared to elsewhere in the study catchment. Also, concentrations that fall in the middle of the range of observations, e.g. Esk at Egton Bridge (0.9 mg l^{-1}), have an intermediate concentration level of both moorland and improved pasture/arable. Thus, it can be stated that SCIMAP reinforces and fortifies the claim of land cover being the dominant driver to catchment water quality parameters with improved pasture being a high risk pollution environment.

In addition, SCIMAP allows the generation of a risk map for the whole catchment which enables the estimation of a risk of high in-stream nutrient concentrations (as outlined in Chapter 3). This in turn allows hot spot catchments and tributaries within these catchments to be identified. The model has been run without accounting for the erosive potential (stream power) and this condition is used here as it resulted in a better optimum model performance and more positive correlation runs in the initial investigation, as shown by the denser dotty plots (Figure 6.1 and 6.2 versus Figure 6.3 and 6.4). Figure 6.5 and 6.6 display the risk maps for (a) nitrate and (b) potassium for the whole Esk catchment.

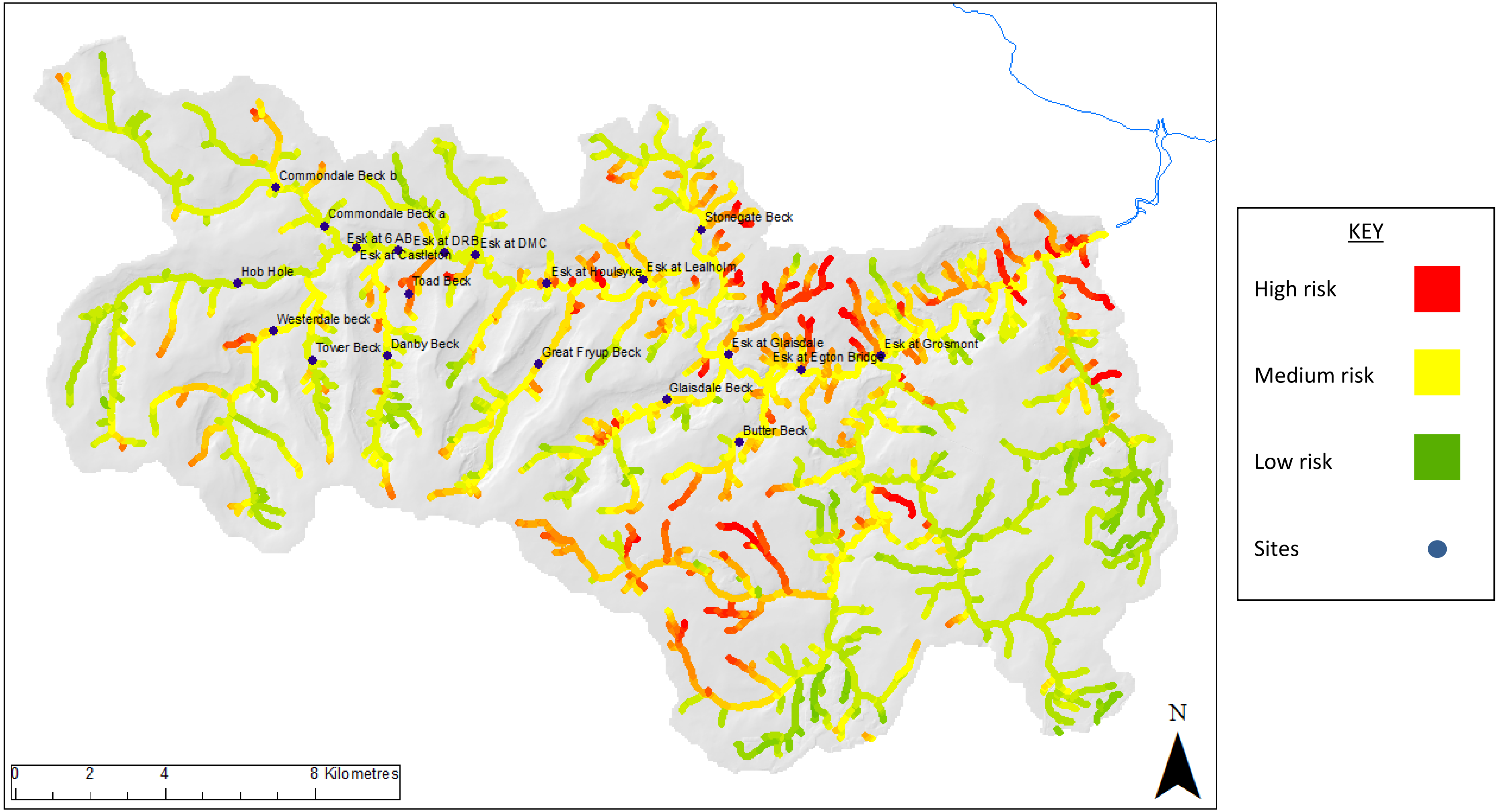


Figure 6.5: Risk map for nitrate (with no stream power) in the Esk catchment

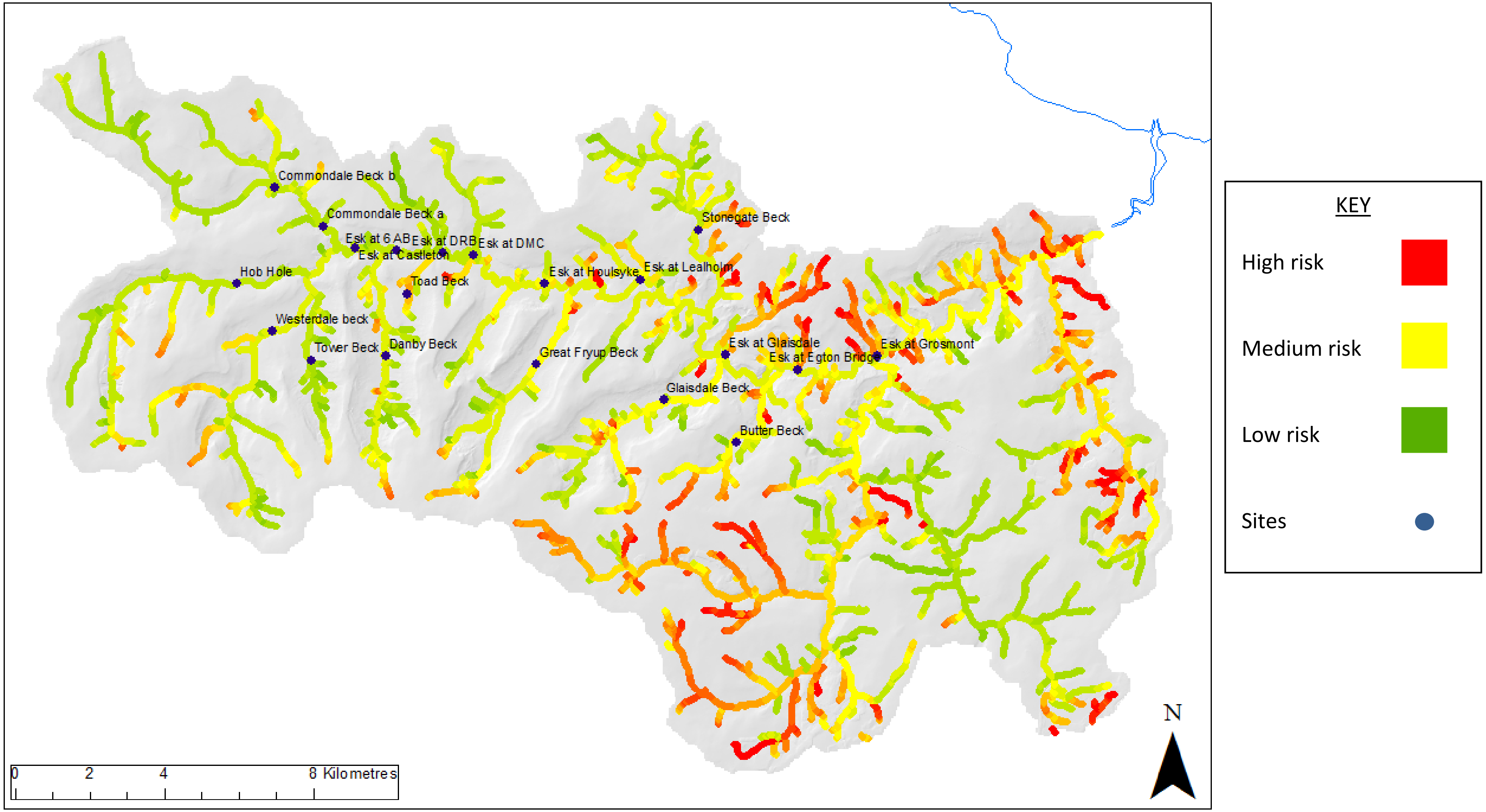


Figure 6.6: Risk map for potassium (with no stream power) in the Esk catchment

Figure 6.5 and 6.6 reveal areas at risk of pollution in the Esk catchment. SCIMAP allows for the prioritisation of areas of concern. Firstly, areas such as the Commondale Beck catchment and Hob Hole catchment can be highlighted as low risk areas and so as low priority for intervention. However SCIMAP does reveal the high risk areas, deduced from empirical data, within the catchment and moves to validate problematic areas revealed in this study. When comparing Figure 6.5 and 6.6 differences in risk can be noted; for example, the Murk Esk catchment in the south-eastern region of the Esk's catchment, not monitored in this study due to this area not containing freshwater pearl mussels, highlights difference in the relative risks. Comparing Tributaries in Figure 6.6 reveal areas of higher risk and at the same point on Figure 6.5 show a lower risk.

When looking at areas covered within the monthly monitoring strategy Toad Beck has a relatively high risk for nutrient concentrations (see Figure 6.5 and 6.6) and is in an area with a large amount of improved pasture, as seen on Figure 3.3. Stonegate Beck demonstrates a similar pattern; however, it does not appear to have high risk areas everywhere in its catchment. In the Stonegate Beck catchment there are particular sub-tributaries that can be identified as having high risk; this is especially notable for the nitrate risk (Figure 6.5). Higher risks in these areas are then diluted as they move down the river network through mixing with other parts of the catchment. Yet as the empirical study found high concentrations at the confluence of Stonegate Beck with the Esk, it suggests that if management is undertaken in these areas the catchment's water quality will improve. This will in turn contribute to an improvement in the water quality in the Esk downstream of this tributary. Areas of the catchment such as the Commondale Beck and Hob Hole tributaries reveal low risk reaches for nitrate and potassium concentrations. Figure 3.3 shows that the Commondale and Hob Hole catchments, particularly the upper headwaters, are dominated by moorland which with empirical data demonstrated relationships showing this pattern to be a reasonable expectation.

This output from SCIMAP allows for the prediction of other hot spots of nutrient concentrations that may dictate and influence the water quality in the catchment. For example, the tributary system east of Stonegate Beck which is a mix of two systems, Cold Keld Beck and Laverick Dale Beck can be identified as high risk hot spot areas. Cold Keld Beck and its tributaries in particular display high risk reaches with predicted high in-stream nutrient concentrations. This area is identified as a hot spot as improved pasture can be found in the locality of the systems (see Figure 3.3). These systems and others like it are worthy sites for the instigation of on-ground examination and collection of empirical evidence to confirm and validate the model predictions.

At a smaller scale, downstream of the Esk at Houlsyke site and upstream of the Lealholm site, a minor tributary can be identified with high nitrate and potassium risk. As this location is upstream of Lealholm, a recognised freshwater pearl mussel habitat (Killeen, 2009), it would be a threatening location to have high nutrient concentrations contributing to the system. Again sampling at this location and in the main stem to see the extent of dilution would test this prediction of a high risk zone. Upon empirical confirmation intervening management could be undertaken to reduce the potential impact of this minor system on pearl mussel habitat in the immediate locality.

6.3 Summary

This chapter uses the hydrological model SCIMAP to account for the concept of hydrological connectivity. Firstly, this work has validated results from the empirical element of the research showing improved pasture and arable land covers are of higher risk to the water quality than other land covers like moorland. Secondly, risk maps (without stream power) were generated for potassium and nitrate to give an impression of and locate potential pollution hotspots in the catchment outside of the areas addressed in the empirical work.

7.0 Discussion

7.1 Introduction

This chapter brings together the findings from the previous results chapters and reviews their implications for basin management. Firstly, the main findings of the study are noted (section 7.2). This material is followed by a discussion of the implications of findings for the freshwater pearl mussel species (section 7.3). Finally, future management options for the River Esk catchment (section 7.4) and the implications for European legislation and directives (section 7.5) are examined.

7.2 Summary of main findings

The analysis of empirical data has revealed a number of interesting points about both the in-stream water quality and the catchment drivers of these trends. In Chapter 4 three particular hot spots of high concentrations were identified: Toad Beck, Danby Beck and Stonegate Beck. Each of these sites displayed high annual mean values of all parameters monitored, especially concentrations of nitrate and potassium. There was a positive trend between nitrate and catchment area in the main stem sites with a low range of concentrations, whilst the tributaries, each with smaller catchment areas, were found to be more variable in terms of nitrate concentration despite their lack of variability in catchment area. These results are comparable to previous published work by Burt and Pinay (2005) who found the same pattern occurring at catchments of greater size (~10^3-10^6 ha) spread over several continents. Results from this study support their work and identify the tributary sub-catchments to be 'polluters' to the main stem system.

Table 7.1: Land cover percentages and annual nitrate concentrations

	Catchment land cover (%)			
Site	Arable	Improved pasture	Moorland	Annual mean nitrate concentration (mg l^{-1})
Danby Beck	7.9	26.6	33.7	1.2
Toad Beck	13.6	49.2	11.7	2.6
Stonegate Beck	14.2	29.4	40.9	1.6
Hob Hole	2.1	3.6	62.0	0.3

The relationship between land cover and the monthly concentrations of selected water quality parameters was assessed (section 4.4), finding significant association between: 1) higher percentages of arable and improved pasture land cover types and high concentrations; and 2) lower percentages of moorland and low concentrations. This trend maps onto and agrees with the hot spot identification tributaries as shown in Table 7.1. Table 7.1 shows the details from 3 hot spots and demonstrates an example of the opposite trend present at Hob Hole, which is almost two-thirds moorland. It seems that land cover is the main driver for the location of hot spots. However, some parts of the catchment will be better connected to the river network than others and this simple empirical relationship between percentage cover and concentration cannot take this into account. The SCIMAP model provided a useful framework to address this consideration in Chapter 6.

The temporal results in Chapter 5 developed the evidence found during the spatial assessment. The hot spots discussed above presented particularly variable trends in water quality parameters over the 8-month sampling period (4-months with the YSI). These areas can be identified as source areas of high nutrient concentrations. Main stem sites downstream of the Esk at Houlsyke demonstrated a consistent trend with reduced variability as the influence of the highly variable tributaries combines to create a consistent signal. The longer-term record (30 months) for nitrate and potassium at Danby Beck and Stonegate Beck showed varying seasonal trends and demonstrated how catchment concentrations can fluctuate depending on the weather conditions. The relationship between nitrate concentration and catchment area over the monthly record established a constant pattern of higher variability in the tributaries (with small catchment areas) and lower variability in the main stem sites (with higher catchment areas). In February, the increased scatter in the record suggests that this is not the definitive driver of nitrate concentration. Nevertheless the consistent trend indicates and agrees with Caraco *et al.* (2003) that the factors driving this variability have more influence in smaller catchments than in larger catchments.

The base level within the Esk revealed constant levels of the anions/cations. High levels of nitrate (over 1 mg l^{-1}) were reported at Lealholm and Grosmont in mid-February even with steady discharge; however, this may be due to high discharge prior to the reduction to consistent baseflow levels. This highlighted the potential importance of ‘old water’ mobilising nitrate and removing it to the channel over an extended period (Kirchner, 2003). Hourly resolution data can also be used to identify relationships between nutrient concentrations and discharge. The nitrate and potassium concentrations both increased in response to the discharge. However, in the case of nitrate, a varying catchment response was noted; at Lealholm the nitrate concentration and stage peaked at the same time, while at Grosmont the nitrate concentrations appeared to lag the stage peak. The driver of these changes was clearly the discharge change, however when considering the drivers over the monthly/ annual scales land cover appears to be significant.

The role of SCIMAP (Chapter 6) proved helpful in both validating empirical work reported earlier and in estimating potential hotspots within the catchment. It was particularly useful to gain an impression of the level of risk (for nitrate and potassium) in tributaries that were not addressed via the empirical work. A number of tributaries (e.g. Cold Keld Beck) were highlighted as potential hotspots and it has been suggested that any further work within the catchment regarding water quality could investigate these areas to validate the model output.

7.3 Implications for the freshwater pearl mussel

Central to the rationale and premise for this study is the presence of a population of freshwater pearl mussels in the River Esk, as set out in Chapter 1. Pearl mussels require clean environments and too much pollution/ high nutrient concentrations can dictate the pattern of population growth/decline (Geist, 2010; Skinner *et al.*, 2003). The spatial component to this study found areas of problematic concentration levels, here termed 'concentration hot spots'. It can be postulated that these are areas of high biogeochemical activity (McClain *et al*., 2003) but it is likely that a number of sub-catchment processes/influences dictated the observed concentrations; in this case land cover has been identified as an important driver. Nitrate and potassium were given attention here due to: 1) their presence in fertilisers; 2) their mobilisation during storms and 3) their implications for the freshwater pearl mussel. In the concentration hot spot areas it can be stated that the freshwater pearl mussel preferred habitat is not present. In the case of nitrate Skinner *et al.* (2003) suggest that nitrate levels should be less than 1.0 mg l^{-1}. Juveniles are more susceptible to these levels than adults and thus ageing populations are prevalent due to habitat degradation, amongst other causes of decline. Therefore, it is fair to hypothesise that the habitat will not be conducive to freshwater pearl mussel development. Sites with annual means of 1.0 mg l^{-1} or greater are shown in Table 7.2.

Table 7.2: Risky areas of freshwater pearl mussels in the Esk catchment

Site	**Annual mean nitrate concentration (mg l^{-1})**
Great Fryup Beck	1.0
Esk at Danby Road Bridge	1.1
Tower Beck	1.1
Danby Beck	1.2
Stonegate Beck	1.6
Toad Beck	2.6

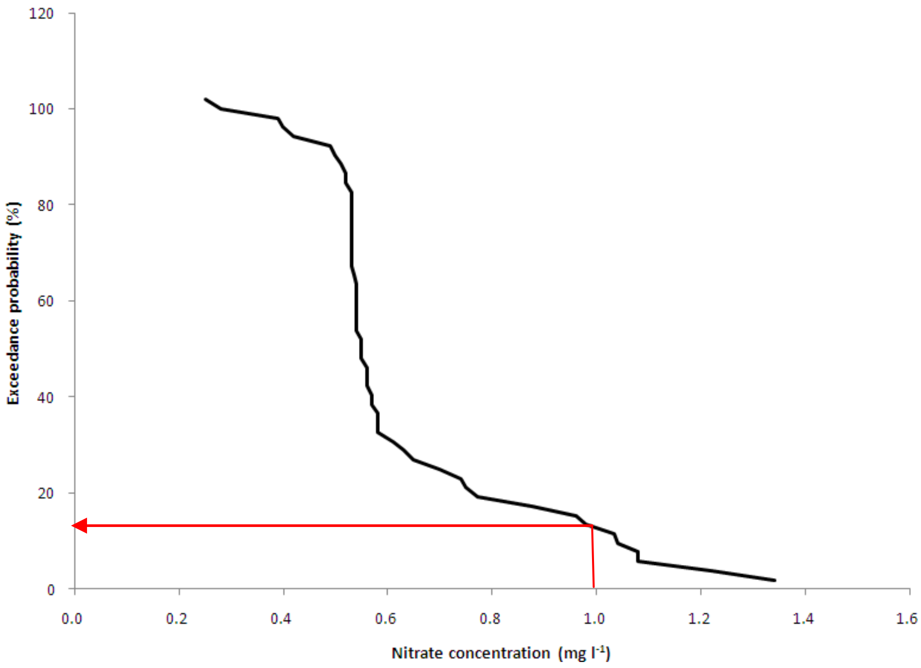
The Esk at Danby Road Bridge site is affected by a reading of 3.3 mg l^{-1} taken in February, otherwise all other values are below the 1 mg l^{-1} threshold. This value may relate to a leaching of old water (Kirchner, 2003) containing high levels of nitrate from the catchment that was mobilised close to the sample date (late February). Secondly, the snowmelt from the heavy winter snowfalls may have influenced the concentrations at this time leading to unusual results. Freshwater pearl mussels according to assessment in 1995 and 1999 (Oliver and Killeen, 1996; Killeen, 1999) are in the main stem between Danby and Glaisdale (NYMNPA Freshwater pearl mussel species action plan, 2008) yet this will by no means be conclusive. For example, personal communication with local landowner (Bargh, personal communication) revealed that healthy pearl mussel grounds are located at the confluence of Great Fryup Beck with the main stem of the Esk. The recent report issued on Esk Pearl Mussel and Salmon Recovery Project (EPMSRP) progress states that the species are present between Esk at 6 Arches (downstream of Castleton) and Glaisdale. Secondly, Simon Hirst, the Project Officer of the EPMSRP, identified a juvenile pearl mussel empty shell (estimated to be 10-15 years old) on the bank of the Esk by Castleton (late May, 2010) (Simon Hirst, personal communication), an area which Killeen (2009) identified to be ‘unsuitable pearl mussel habitat’. Despite not knowing how long the shell was resident there, this evidence of juvenile pearl mussels is encouraging since the majority of the population surveyed are 60+ years old with some ~40 years old (Esk Pearl Mussel and Salmon Recovery Project, 2010a). This distribution and conflicting evidence flags the lack of understanding in habitat requirement for the species. The annual mean nitrate concentration at Lealholm was found to be 0.8 mg l^{-1}; this is a positive outcome as Killeen’s assessment (2009) found this reach of the river to be ‘good pearl mussel habitat’.

The temporal evidence strengthened this argument of concentration hot spots in a number of areas within the catchment. The data sampled at a higher resolution, via autosamplers, showed the concentration reactions to an increase in stage. The event captured mid-March 2010 at Lealholm and Grosmont showed how concentration can be elevated in these periods. A difference in the nature of the response between Lealholm and Grosmont was suggested to be due to a difference in the sources. At Grosmont all samples monitored over the course of the event were over 1.0 mg l^{-1}. There was also an indication in the final samples that a delay in nitrate export had occurred, potentially due to old water contributing via subsurface processes, as concentrations increased to as high as 2.0 mg l^{-1}. At Lealholm there was a more pronounced peak in nitrate at 3.0 mg l^{-1} (three times the limit for pearl mussel survival of 1.0 mg l^{-1} (Skinner *et al.*, 2003)) and ~40% of samples over 2 mg l^{-1}. These nitrate levels at both Grosmont and Lealholm exceed suggested tolerances for the species and will not support an environment where either organisms can survive and multiply or mussels can be re-introduced from the captive breeding programme at

Windermere managed by the Freshwater Biological Association (FBA). Importantly, these higher resolution results show concerning levels in the main stem as opposed to the tributary bound hot spot areas discussed above. An important question that these data raise is the exposure period of elevated nitrate concentrations upon the freshwater pearl mussels? How long must a pearl mussel be exposed to and come into contact with high nitrate concentrations before it is negatively affected? In light of the high resolution autosampler data, will pearl mussels be affected by pulses of nitrate, lasting 12 hours for example, that may be double or even three times the 'normal' levels? Or does the localised nitrate concentration need to be consistently above 1.0 mg l^{-1}, as was the case in monthly resolution monitoring at Toad Beck? If the nitrate level is 1.0 mg l^{-1} or greater over 50% of the time does this affect the species, as was the case at the main stem site at Egton Bridge?

Figure 7.1 utilises the flow duration approach to consider exposure to nitrate. Here the nitrate concentrations recorded from the Danby Moors Centre site from autosamplers, monthly monitoring and secondary data are combined with stage levels from the site. Figure 7.1a displays the relationship between probability of exceedance and all the nitrate concentration data from the Danby Moors Centre located on the Esk. At the 1.0 mg l^{-1} intersection with the curve the data proposes that ~13% of the monitored period the concentration was found to exceed this suggested freshwater pearl mussel habitat preference limit. Assuming that increased stage causes an increased nitrate concentration (Chapter 5) it can be estimated, using Figure 7.1b, that with a stage of ~70 cm there is an increased risk of nitrate concentrations that exceed 1.0 mg l^{-1}.

a.



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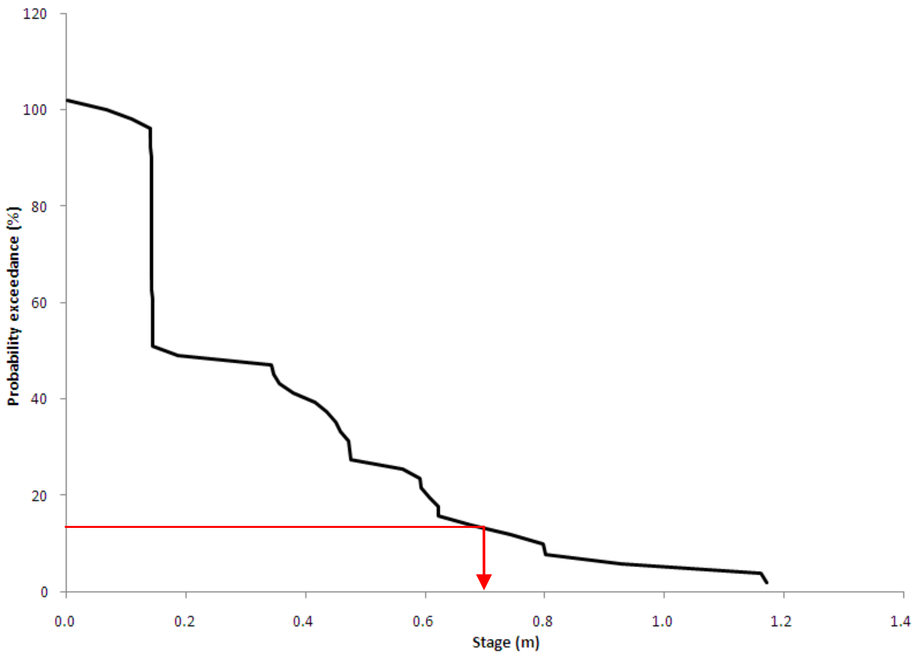

Figure 7.1: Probability exceedance for (a) nitrate concentration at the Esk at Danby Moors Centre and; (b) stage at the Esk at Danby Moors Centre

Figure 7.2 further develops this assertion of a stage threshold association with the pearl mussel nitrate concentration. It displays the flow duration curve for the Danby Moors Centre using daily average stage data from mid-October to early July (the time period of study). If ~13% of samples from Danby Moors Centre exceed 1.0 mg l^{-1} and 13% of the samples exceeded a stage of 70 cm, then to align this with the annual flow duration curve reveals that 23% of the logged period have values resulting in stage records over 70 cm. Therefore it can be suggested that at this site 23% of the time the nitrate concentration exceeds 1.0 mg l^{-1}; is this a viable freshwater pearl mussel habitat?

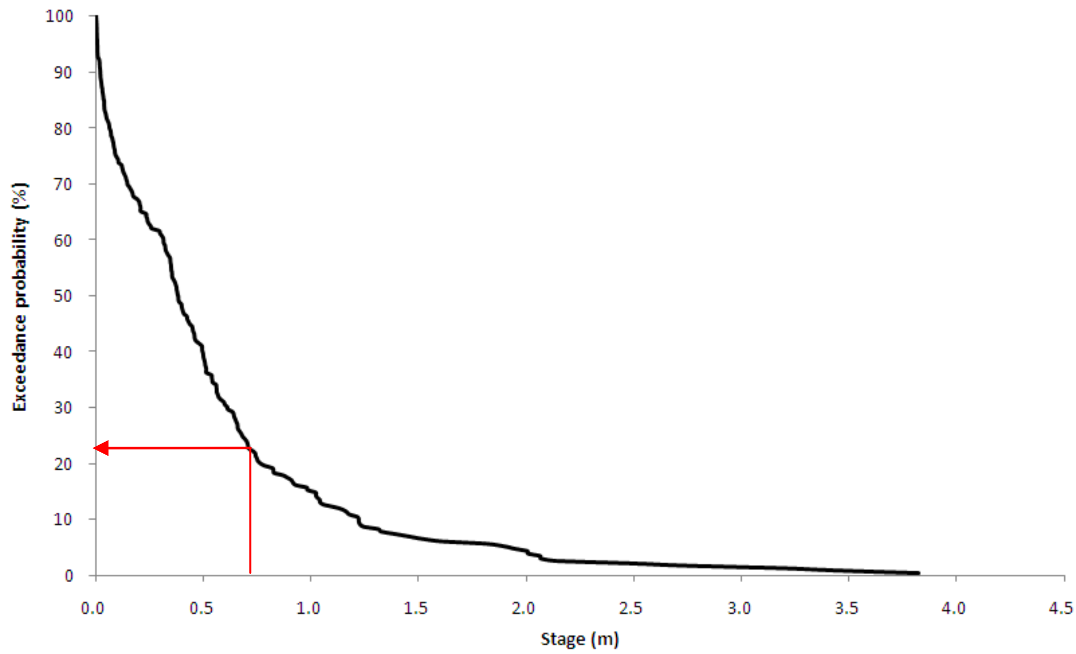

Figure 7.2: Flow duration curve for the Esk at Danby Moors Centre

It must be noted that this approach assumes a consistent relationship between nitrate concentrations and stage. The inference is simplistic but begins the discussion on exposure period concerning levels of monitored parameters, here focussing on nitrate. Secondly, the enquiry into exposure period ensues the questions of the intensity of the exposure period and the extent of the negative influence upon the species. Is the nitrate concentration worse for the species at 5.0 mg l^{-1} than 1.0 mg l^{-1}? It is a fair assumption to assume that it is. However, tied to this is the extent of the negative impact upon the species: how do varying levels of nitrate affect the freshwater pearl mussel? These are questions that are not within the remit of this study but they should be on the agenda for those concerned for the conservation and survival of the freshwater pearl mussel. The spatial and temporal variations in water quality do reveal areas of concern within the catchment and to aid the protection of the pearl mussel governing bodies must look at management options to reduce in-stream concentrations.

7.4 Future management options for the River Esk catchment

This research has identified a number of areas where management can be focussed to improve water quality and pearl mussel habitat. These areas, or sub-catchments, were identified to be Danby Beck, Toad Beck, Stonegate Beck (and to a lesser extent, Great Fryup Beck). These areas have been termed hot spots due to the high concentrations monitored there within the study period. The primary driver of the concentrations focussed on here was found to be the catchment land cover and this finding has been reinforced with the use of SCIMAP (section 6.3). Therefore a focus on land management is likely to yield improvements in water quality.

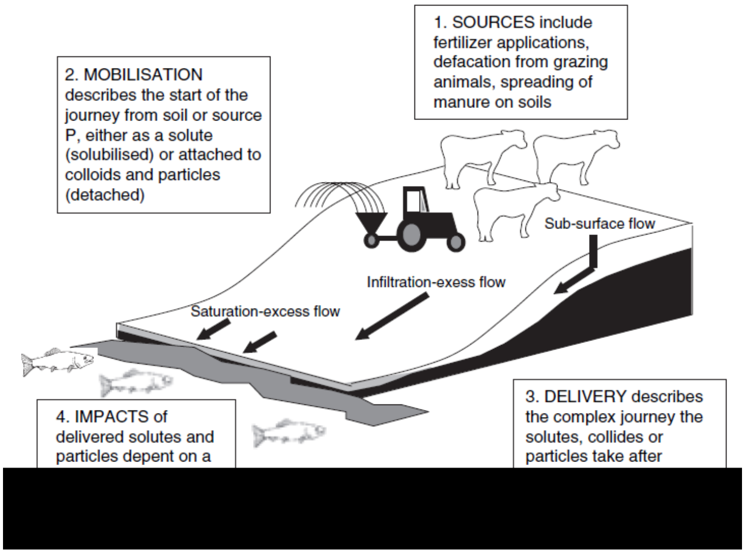

Figure 7.3: Sources-mobilisation-delivery-impacts framework (from Withers and Haygarth, 2007).

Figure 7.3 conceptualises the manner with which nutrients are sourced, mobilised and transferred through an agricultural system. This is followed by the impacts phase upon the biotic and abiotic processes within the water (Withers and Haygarth, 2007). This concept will form the framing of the following discussion that addresses and suggests land management techniques that could be implemented to achieve improved water quality in the Esk catchment. In the Esk study the impact is reduced water quality and higher concentrations of certain anions and cations that affect the habitat of the freshwater pearl mussel. Land management should be a priority to aid the improvement of the species habitat. Vidon *et al.* (2010) and Cuttle *et al.* (2007) will be central review articles to this section.

Firstly, all the positive work and land management methods used in the Esk should be acknowledged. The Esk Pearl Mussel and Salmon Recovery Project (EPMSRP) have co-ordinated much work with the objective of protecting the threatened salmon and freshwater pearl mussel populations. For example, recently LEADER funded work has reached completion with different forms of river restoration works completed in 21 farms in the catchment (Esk Pearl Mussel and Salmon Recovery Project, 2010b). Table 6.3 provides an overview of the mechanisms addressed by this work.

Table 7.3: LEADER funded river restoration work in the Esk catchment (Esk Pearl Mussel and Salmon Recovery Project, 2010a)

Mechanism	**Amount**
River bank fencing	~20 000 m
Buffer strip creation	2-10 m (either side of river)
Native tree planting	1160 broad leaved trees
Tree management	6 days of work
Construction of cattle crossing points	7 sites
Alternative livestock water provision	16 new installations
Gate improvement works by river	6 sites

It is hopeful that the measures that habitat suitability for pearl mussels (and salmon) in the Esk will improve. However following empirical assessment of the in-stream water quality it is worthwhile to look at land management techniques and alternative mechanisms that may be suitably applied in certain hot spots from a 'source', 'mobilisation' and 'delivery' framing.

Toad Beck is the catchment that the empirical element of the study revealed to have the highest concentrations of many ions. It is a relatively small catchment, with an area of 1.8 km^2 so intervention will be easier to implement and management costs potentially smaller than in other locations. Toad Beck has ~14% arable land cover within its catchment, which is one of the highest levels calculated in-terms of upstream land cover proportions, therefore it is worth considering how this land is managed. At a 'source' level the conversion of arable land to extensive grassland and reducing fertiliser application rates are options to minimise nutrient sources (Cuttle *et al.*, 2007). Around 50% of the catchment is improved pasture so at both a 'source' and 'mobilisation' level encouraging farmers to reduce stocking densities (especially when the soils are wet) would positively impact nutrient load in the tributary water quality. Danby Beck and Stonegate Beck, both slightly larger tributaries to the main stem (12 km^2 and 14 km^2 respectively), are areas where similar mechanisms could be investigated. Both have relatively high percentages of arable land (8% and 14%) and improved pasture (27% and 29%) so these mechanisms are options to be considered although specific areas may need to be identified.

A management technique to use in all hot spot catchments which operates at the 'delivery' phase would be the use (or greater use) of vegetation buffer zones. Riparian landscapes have been identified as natural buffers due to the recognition of the fact that they can remove nutrients that move through the system (Burt, 1997; Gilliam *et al.*, 1997; Vidon *et al.*, 2010). They are key to in-stream concentrations as they are located at 'the interface of upland and aquatic ecosystems where intersecting hydrologic flow paths produce dynamic moisture and biogeochemical conditions' (Vidon *et al.*, 2010: 279). Uusi-Kämppä and Ylaranta (1992) found grass buffer strips to reduce nitrogen load by 47% over an annual cycle in Finland. Parameters such as nitrate vary over time and thus there are periods when loading in the riparian zone are greater, for example during rainfall or snowmelt (Vidon *et al.*, 2010). This was exhibited in this work by varying nutrient levels found in February (post winter snowfalls and melt period). To combat high concentrations in-stream riparian buffers are an option to not only improve in-stream water quality but also the water quality within the sub-surface zone (Gilliam *et al.*, 1997). An additional recommendation for buffer strips that are new or old would be to harvest buffer zones to reduce the nitrogen component stored there to decrease 'the risk of...nitrogen leaching outside the growing season' (Räty *et al.*, 2010). The debate about riparian buffer width is complicated, yet Vidon and Hill (2006) compile data from a range of studies to suggest that a width under 20 m can be adequate to remove nitrate in most cases. Therefore the addition of these systems in the hot spot sub-catchments would be effective to this end. Greater use within the three identified catchments would support the ambition for better in-stream water quality. In all cases the field assessment and suitability combined with cooperation of land managers would need to occur to ensure effective implementation. The use of buffer strips may have been encouraged throughout the Esk via the bank fencing work carried out by the EPMSRP but the hotspot catchments should be assessed for whether there is the potential to add any more buffer strips or wider strips to help improved water quality in the river system.

Vidon *et al.* (2010) outline a number of other 'delivery' level management options that could be utilised in the riparian zone to reduce nutrient mobility. These options are potentially more costly yet may be worthwhile in locations such as Toad Beck where a significant problem has been identified in a relatively small catchment. Firstly, riparian walls of denitrifying material, e.g. organic matter, in trenches located in problem areas. The function of organic matter is to decrease the oxygen availability by encouraging the process of aerobic respiration and also to promote the activity of denitrifying bacteria via the provision of carbon (Schipper *et al.*, 2005); materials that can be used are wood mulch and leaf compost (Robertson *et al.*, 2000). These walls will absorb nitrate from subsurface flows and denitrify the anion back to nitrogen (N_2) and have been employed to combat pollution from 'septic systems, agricultural runoff, landfill leachate, and industrial operations' (Robertson *et al.*, 2000: 689). The experimental work of Schipper and Vojvodic-Vukovic (2000: 269) in New Zealand found that 'denitrification rates (0.6-18.1 ng cm^{-3} h^{-1}) were generally high enough to account for the nitrate losses in groundwater (0.8-12.8 ng N cm^{-3} h^{-1})'. Schipper *et al.* (2005: 1270) found a limitation to denitrifying activity to be 'attributed to nitrate predominantly moving through zones of greater hydraulic conductivity or in the mobile fraction of the ground water and slow diffusion to the immobile fraction where denitrifiers were active'. Thus, to begin to overcome this problem and to form an effective use of this technique, information on nitrate load and the rate of nitrate removal from ground water flow rates would need to be deduced within Toad Beck (Schipper *et al.*, 2005). Secondly, another mechanism that can be used within the active riparian zone is 'permeable reactive barriers to remove contaminants such as NO_3^- and trace metals from tile drains and subsurface flows' (Vidon *et al.* 2010: 290). However a key focus of this technique is to remove trace metals (Blowes *et al.*, 2000) and so this may not be appropriate in the Esk hot spots.

In hot spot regions tile drains, added to cultivated agricultural land typically throughout the twentieth century, are likely to be present. These systems aim to remove water from fields more quickly than by simply natural infiltration and subsurface flow processes. Deasy *et al.* (2010) noted that they are significant routing mechanisms for sediment through to the river system, which therefore may have entrained nutrients attached. They therefore have a significant role at the 'delivery' level in the system. However the depth of these tile drains can be such that nutrients including nitrate can be absorbed before it is received into the drainage system. Heathwaite *et al.* (2006) found, particularly with relation to phosphorus, that tile drains could result in significant concentrations delivered out of the soil zone. Thus the question of how beneficial these systems are to the water quality and the habitat of the freshwater pearl mussel should be considered. This question and the importance of tile drains can be asked of the catchment as a whole, but effort should be particularly focussed to assess the extent of drainage in the identified hot spot areas.

Essentially, Toad Beck, Stonegate Beck and Danby Beck are targets for land management based on the empirical study here and validation from SCIMAP. Work completed thus far, for example the LEADER funded work, is an excellent foundation. These installations should be maintained so they operate effectively and work of this nature should be up kept and alternative mechanisms implemented in suitable areas. Toad Beck is a relatively small catchment with high pollution levels and so it should be a priority for further work. Mechanisms discussed above should be implemented in effective locations. In the Danby Beck and Stonegate Beck catchments drainage extent and transport pathways should be investigated and mechanisms discussed above employed.

7.5 Implications for European legislation/directives

This work must be considered in a wider context of directives that frame multiple objectives for managing river systems. The Water Framework Directive (2000/60/EC) (WFD) aims to 'ensure sustainable management of groundwater, freshwater and marine water in the European Union, such that good ecological quality of all such water bodies will be obtained by 2015' (Carstenen, 2007: 3). A key focus of this directive are nutrients as they are the major driver of eutrophication in surface waters (Hilton *et al.*, 2006). Interestingly, Hilton *et al.* (2006) draw what they call ‘retention time’ into question; this relates to the residence time of nutrients to enable the planktonic algae to use the supply to their benefit. This exhibits parallels with the concept of exposure time developed in section 6.4; it therefore appears that understanding the impact of nutrients upon the river system, in terms of the affect that this can have in light of the WFD and its aims, is a key question. The threatened population of freshwater pearl mussels in the Esk river, now estimated to be 1000-1500 individuals (Esk Pearl Mussel and Salmon Recovery Project, 2010b), suggests that the river is not meeting the requirements of the directive as it cannot support its indigenous natural population with correct habitat. Age estimation suggests that the majority of this population are ~60 years old and over, yet some are 40 years old which shows that the successful breeding occurred in the early 1970’s. Therefore, it is over the past 40 years that changes in habitat have resulted in species decline and made the directives target of maintaining the ecological sustainability less achievable.

The Biodiversity Action Plan (BAP) is also a consideration for the freshwater pearl mussel species *Margaritifera margaritifera*. Nationally it is listed on the UK BAP as a priority species (www.ukbap.org.uk). The North York Moors National Park Authority (NYMNPA) have devised a species action plan that aims ‘to halt the decline of the freshwater pearl mussel population in the River Esk’ (NYMNPA Freshwater pearl mussel species action plan, 2008: 1). Progress since the start of this project (2006) is encouraging and work completed by NYMNPA and the EPMSRP should maintained to advance attempts to achieve the goals set by directives. Catchment Sensitive Farming (CSF) plays a role in achieving this target. A number of other mechanisms are targeted to seek improvement in the species habitat in the Esk catchment as discussed below.

A number of financial resources and mechanisms have been initiated to achieve this goal. Entry Level Stewardship (ELS) and Higher Level Stewardship (HLS) schemes are agri-environments programmes that have been in operation for the past 5 years to take the place of Environmentally Sensitive Areas (ESAs) and the Countryside Stewardship scheme (CSS) (Hodge and Reader, 2010). Agri-environment mechanisms are methods to financially compensate farmers for changes that they make to their land to strive towards the aims set be directives such as the WFD (Kleijn and Sutherland, 2003). These programmes will prove essential to the success of the rehabilitation of the water quality in the Esk and its catchments. Good work to this end is already in operation in the Esk catchment as the Project Officer of the Esk Pearl Mussel and Salmon Recovery Project is liaising with Natural England staff making efforts to promote the use of ELS and HLS schemes. For, example, HLS has been undertaken by four farms in the Esk catchment since summer September 2010 and a further 8 farms have been proposed to Natural England as potential HLS farms; CSF grants were given to 8 farmers in the Esk catchment in 2009/2010 (Simon Hirst, personal communication). This work should continue and plans made for the upkeep of the work achieved by the schemes as land management is a continual process.

Cross-institution work by the North York Moors National Park Authority (NYMNPA) with the EA and Natural England (NE) are vital to this end. The ESPMRP group has provided an environment that harbours a wealth of both local and specialist knowledge with committee members from multiple organisations. This group illustrates an excellent example to stakeholders in other areas of how a nexus of influence and resources can communicate and operate together to positively affect the environmental issues. The institutional arrangement to enable successful joint mobilisation to this end is key to effective instalment of management plans within the catchment. The current governmental-driven budget cuts on the horizon highlight the reason that it is important to maintain cross-institutional work so distribution of resources and knowledge is preserved and allows for the pursuit of the goals set by the directives, such as the WFD, and the habitat improvement for the freshwater pearl mussel to continue. Work on the ground with landowners, farmers and the public by members of these listed organisations is essential to build confidence in and knowledge of the schemes among the stakeholders. This has particular emphasis to landowners and farmers who, in many cases, have livelihoods that exist on the basis of the land. Attitudes towards land management schemes must be treated as an issue alongside the science of the known problems facing the Esk to ensure mitigation is successful. An example of this is the recently published 'Water Friendly' Farming Guide that is a resource for local farmers which raises awareness of the issue facing the resident pearl mussel population and highlighting the ways they could help the cause.

<u>Summary 7.6</u>

This chapter has given an overview of the issues surrounding the survival of freshwater pearl mussel. Primarily of interest are the identified hot spots that have been validated via the use of the risk-based hydrological model SCIMAP, and the mechanisms that could be employed or expanded to improve the local in-stream water quality. SCIMAP furthered empirical work by estimating the location of other potential hot spots within the catchment. An issue flagged in section 7.3, indicates that the exposure period of the species to high nutrient content is central to future work. Finally, this chapter focuses on the efforts to meet directives and efforts that can be made to manage the poor water quality located in hot spot catchments. Cross-institutional mobilisation is highlighted as key to the issue and the work to improve water quality; this should be operated and encouraged as a primary strategy in other catchments facing biodiversity problems.

8.0 Conclusion

8.1 Central conclusions

This work aimed to address the spatial and temporal trends in water quality parameters in the Esk catchment in relation to the freshwater pearl mussel population. The point sampling network spatial survey addressed the first objective and revealed a number of tributaries and sub-catchments that had high parameter concentrations. These catchments were identified to be Danby Beck, Toad Beck and Stonegate Beck. Nitrate is a nutrient of particular concern, with respect to the freshwater pearl mussel, with the annual mean concentrations in each of these tributaries found to exceed the 1.0 mg l^{-1} threshold postulated as important in the pearl mussel literature (Skinner *et al.*, 2003). In relation to the second objective potential drivers of this pattern of concentrations of parameters were investigated; land cover was found to be the dominant driver. In general, the higher the percentage of arable land and improved grassland in the upstream catchment, the higher the annual mean concentration of monitored anions and cations. Moorland land cover demonstrated the inverse trend with lower concentrations when percentages were higher.

Further addressing the first objective temporal data, collected from autosamplers, revealed that stage (and thus discharge) can often have a notable influence on water quality. Data highlighted the importance of sub-surface contributions to the river network; this equates to the input of 'old water' as postulated by Kirchner (2003). When the water quality was captured during an increase in stage, an increase in parameters such as nitrate and potassium concentrations was observed. All nitrate concentrations were greater than the 1.0 mg l^{-1} limit that Skinner *et al* (2003) suggest; with maximum concentrations of 3.0 mg l^{-1} recorded at Lealholm, a site noted by Killeen (2009) to have good pearl mussel habitat. These data raise the fundamental question of the impact of exposure time to raised concentrations. The duration of exposure must be targeted as a research goal by freshwater pearl mussel scientists.

This work was developed by the application of the hydrological risk model SCIMAP. The model begins to account for the process of hydrological connectivity that is not addressed in earlier work. The model results highlighted other hot spot areas within the catchment that, based on their land cover and topographic characteristics, could hold implications for the water quality and in turn the freshwater pearl mussel population. The reported results are interesting yet require validation to begin to confirm the risk predictions it raises.

This empirical and modelling evidence identified areas of the catchment that were hot spots and where resources should be targeted to help efforts to conserve freshwater pearl mussels, addressing the fourth objective. Changes in management practice in line with those suggested for the hot spot areas (e.g. the addition/expansion of riparian buffer zones) has potential to improve the catchment water quality.

8.2 Limitations to study

There were a number of limitations to this study that reduce the research's potential to meet the aim of the work. A major limitation to this study was related to the temporal aspect. Monthly sampling was conducted over an 8-month period; if it had been possible to sample over the other 4-months of the year, then a complete annual mean dataset would have been generated which would have provided a more complete picture of the annual cycle. Secondly, if the sampling period could have been extended over multiple years, a greater impression of the seasonality would have been gained. Fortunately, it was possible to look at the seasonal pattern by utilising secondary data (from Bracken, 2009), yet the same spatial coverage as conducted in this study with a longer record at all sites would provide more robust data for seasonal analysis. Thirdly, it there were difficulties capturing the water quality signal during stage increases. This could be due to battery failure or simply dry periods.

Sample frequency was limited by time that could be spent in the field whilst maintaining a manageable spatial coverage. The majority of the main tributaries were sampled, yet with more time available a higher sample frequency would have provided a more detailed impression of the spatial variations in water quality parameters. Indeed, the use of SCIMAP revealed a number of 'high risk' tributaries that were not sampled in the created sampling strategy.

Samples were tested as soon as possible following collection in the field yet this sometimes incurred an overnight period which would allow any bacteria present in the sample to begin to alter the chemistry prior to analysis. The Dionex has low detection levels yet still limits the ability for low concentrations to be monitored; it would be particularly helpful if the equipment detected lower levels of phosphorus.

8.3 Suggested further work

This work has taken steps towards the improvement of the River Esk habitat for pearl mussels via the assessment of spatial and temporal water quality in the catchment. Suggested work during the future should be undertaken in the identified sub-catchments found to be concentration hot spots. Further monitoring should be carried out in these sub-catchments (Danby Beck, Toad Beck and Stonegate Beck). Yet further actions should be taken in these sub-catchments; key landowners should be identified and made aware of the water quality problems; the current land management practices should be reviewed; and buffer zones should be assessed for either initiation or expansion. Secondly, this work has dealt specifically with hot spots, but further work within the catchments, perhaps initially in the hot spot zones, to begin to investigate the presence (or absence) of hot moments that McClain *et al.* (2003) discuss would be helpful. This aim would link to the drive for an improved picture of catchment seasonality in the water quality.

SCIMAP identified, based on topography and land cover, high-risk areas within the catchment. Areas that are estimated to be of particularly high risk to the water quality should be monitored and the land management practices assessed. This work would validate the model results; for example, Cold Keld Beck, north of the main stem was clearly identified to be an area of high risk, this could be a priority for assessment in the future.

This work has highlighted the question of exposure time of the pearl mussel species to solute concentrations. Continued liaison with scientists at the Freshwater Biological Association (FBA) and other specialists regarding freshwater pearl mussel water quality requirements would provide a mechanism with the relevant knowledge-base to come to terms with this question and investigate the mechanism to tackle this issue. Further data from autosamplers would extend the information on the response of water quality to changes in stage.

The Esk has benefitted greatly from the work of the Esk Pearl Mussel and Salmon Recovery Project (EPMSRP). Work ranges from a grassroots level of working at educating young people in local schools of the presence of pearl mussels, to work with local landowners and farmers in respect to land management practices and the issues the catchment is facing. Work such as the River Esk Water Friendly Farming Guide is an example to this end. The joint institutional work between the North York Moors National Park Authority (NYMNPA), Environment Agency and Natural England as part of this cluster of knowledge and resources is to be commended and supported. Their influence to promote work such as the Catchment Sensitive Farming Programme, Entry Level Stewardship/Higher Level Stewardship should not be underestimated. Such management programmes should be maintained and encouraged to the extent made possible in light of current government budget cuts and climate of financial uncertainty. This will help to tackle the issue of diffuse pollution within the catchment therefore, improving the habitat for the currently endangered freshwater pearl mussel population.

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